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MODERN CHEMISTRY

THE ROMANCE OF MODERN CHEMICAL DISCOVERIES

BY

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PREFACE

THE object of this book is to provide an account of some of the more important and interesting discoveries of chemical science and of their applications. As far as possible it has been written in language shorn of technicalities, so that it may be intelligible to the cultured general reader. Since the war there has been a deep and widespread interest in the problems and achievements of the chemist. There exists to-day a large public, alive to the importance of chemistry in our national life, but with no time or inclination for mastering the principles and details of the science. It is for this section of the reading public that the author has written. In addition the book should prove useful supplementary reading for chemistry students in schools or colleges, although it is definitely not a text-book. The subject matter is discussed from both the theoretical and practical point of view, but in most chapters the everyday life aspect is kept in the foreground.

The author would like to return his most grateful thanks to his wife, to Mr. J. A. Mitchell, M.Sc., and to Dr. F. Matthews, for reading the manuscript and proof sheets and for information, advice and suggestions; and to the numerous companies and individuals who have supplied illustrations. I have also to thank Messrs. Arnold and Co. for permission to reproduce a diagram on the manufacture of coal gas and Messrs. J. and A. Churchill for the three illustrations on pp. 195, 205 and 206.

The chymists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapour, soot and flame, poisons and poverty. Yet among all these evils I seem to live so sweetly that may I die I would not change places with the Persian king.

—J. J. BECHER, *Physica Subterranea* (1669).

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MODERN CHEMISTRY

CHAPTER I

THE SCOPE AND DEVELOPMENT OF CHEMISTRY

It has been said that the aim of science is to acquire as complete a knowledge as possible of the material universe. But he would be a bold man who would claim, as did Francis Bacon in the seventeenth century, to take all knowledge as his province. The scientist of to-day is essentially a specialist and although he may, and indeed should, take an intelligent interest in all branches of science, he can only become a master of little more than a fragment of scientific knowledge. With the rapid advance of modern science it has become necessary for investigators to limit the range of their studies, and a classification of our knowledge of the material universe has become not only a matter of convenience, but of necessity. This classification of science into different branches is merely one of convenience; it facilitates study and makes progress easier. But it is not inherent in nature. On the contrary, scientific knowledge forms an undivided whole. While each branch of science has certain characteristics and looks at nature from some special aspect, it is not isolated from the other branches. Indeed, new discoveries in one science often illuminate the problems of another.

The science of chemistry is mainly concerned with the composition of matter; physics studies those properties of matter capable of exact measurement; geology deals with the structure, composition and history of the earth's crust. These are sometimes referred to as the physical sciences. The biological sciences which include zoology, botany and physiology, study the behaviour of matter in its association with life and the phenomena observed in the living organism.

Chemistry is the science which deals with all forms of matter constituting the material universe. It examines the different kinds of substances found on the globe, whether they are obtained from non-living mineral matter or from living things, and it probes into their composition and methods of preparation. Chemistry also investigates the phenomena which occur when these different types of matter react with one another, and when such physical agencies as heat, electricity and light act upon them. The chemist is able to transform substances, useless in their natural state, into products of real value. Moreover, he can prepare in the laboratory substances that are normally produced by the activity of animal and vegetable organisms. Chemistry is not only concerned with the conversion of raw materials into valuable products, but it investigates the manner in which this conversion can be most economically effected. The chemist keeps a check on nature's storehouse; he prevents it from being plundered by the ignorant and the unscrupulous. Chemistry is largely an experimental science. Indeed, it would have made little progress if it had been content to observe phenomena just as they occur in nature. By experiment it is possible to make combinations of different forces, and different forms of matter that do not occur in nature. Drugs, dyes and textiles do not occur ready made in nature; they are products of the chemist's art.

The aim of chemistry is not only utilitarian. The chemist, occupied as he is with the transformations of matter, experiences an intellectual and spiritual satisfaction in his search for truth. He is forced to look below the surface of things, and to reflect upon the ultimate constitution and structure of matter. He realises that the forces controlling the changes in his laboratory also operate on a large scale in nature's laboratory; the microcosm epitomises the macrocosm. The Earl of Balfour in an address to the Society of Chemical Industry remarked:

> Chemistry is not merely a great science among the sciences, but a science that permeates the whole of life. The greatest of all aspects of scientific study is the discovery of how the world we live in is constructed; what its real, intimate character is.

Since the dividing line between the sciences is purely artificial it is not surprising to find that many of the problems of physics, botany, geology, physiology and medicine are essentially chemical. The physicist depends on the chemist for the glass and metal of his instruments, for the mercury in his thermometers and barometers, and for his source of light and heat, whether this be gas or electricity. The physiologist, who deals with the vital processes going on in the living organism, realises that these are essentially chemical ones. Respiration, digestion, nutrition and the excretion of waste products are manifestations of chemical change. The geologist requires a knowledge of chemistry when he examines the substances present in the earth's crust, or when he studies the action of air, heat and water on rocks. His tests for minerals depend on specific chemical reactions. Even the astronomer has recourse to the instruments of the chemist in his survey of the heavens.

During the examination of a substance the chemist constantly asks himself "Of what is it made?" and "What can be made from it?" Very often an answer to the first question supplies an answer to the second. One way to understand how a clock works is to take it to pieces, and to put the parts together again. An analogous method is employed by the chemist when he investigates the composition of a substance. He can break it up or analyse it into simpler substances with which he is already familiar, and in this way gain some idea of its nature. For example, cane sugar can be broken up into carbon, hydrogen and oxygen, three elements with which the chemist is quite familiar, and by special analytical methods he can deduce the proportion in which these elements are present. Now the opposite process—the building up or synthesis of sugar from simpler substances—can be done, but it is far more difficult. As a rule it is much easier to analyse a substance than to synthesise it. The first analysis of cane sugar was made in 1814; it was not synthesised until 1899. Those who have tried will know that it is much easier to take a clock to pieces than to put it together again. Some substances resist all attempts to resolve them into anything simpler; they are called elements. There are also some substances derived from living matter that the chemist has not yet synthesised, e.g. insulin, chlorophyll (the green colouring matter of plants) and the vitamins. Many changes are going on in nature, in our own bodies for example, that cannot be imitated in the chemical laboratory. Even when the chemist does succeed in synthesising substances that are produced by living animals or plants he often has to do it by roundabout methods involving the use of high temperatures and pressures, and of chemicals that are never found in animals or plants.

As outlined above, chemistry seems very remote from the industrial operations popularly associated with it. It must be remembered, however, that the work of the chemist in industry is based upon certain scientific principles that have been developed during the last hundred years or so. Chemists do not always set out with the idea of making discoveries and inventions that will have an immediate application in industry. Indeed, the fundamental discoveries in chemistry, and for that matter, in all branches of science, have been made by those interested in scientific work for its own sake. Many an industry has sprung from the patient research work of chemists who had no thought of its industrial application; they were interested in research for its own sake. The synthetic colour industry had its origin in the research work of Sir William Perkin, who, in attempting to synthesise quinine, made a chance discovery that led to the preparation of many artificial dyes. As far back as 1829 Sir Humphry Davy wrote:

> The mechanical and chemical manufacturer has rarely discovered anything. He has merely applied what the philosopher has made known, he has merely worked upon the materials supplied to him.

The position is much the same to-day. It is only rarely that the same individual has the talent for discovery and invention —that is, the application of discoveries to material needs. Discovery and invention are complementary. The successful commercial application of the results of scientific research undoubtedly requires the exercise of much skill and ingenuity and often the laying out of considerable sums of money. It is the industrialist who has made the scientist's discoveries of service to the public, but in doing so he has usually exploited both the scientist and the public. Very often the scientific investigator who has created a world-wide industry has received little or no financial recognition. In fact Faraday, to whom we owe the uses of electricity in lighting, communication and industrial electric power, refused any financial reward for his work, and Perkin only received a knighthood for his researches on dyes. The Government found this form of recognition much cheaper than an annual research grant.

The importance of scientific research in industry cannot be over-estimated. To-day all the important industries employ a scientific staff trained in research and able to apply their own discoveries to the industry in which they are employed. In his presidential address to the British Association in 1926, the Prince of Wales remarked:

> Scientific research, properly applied and carried out, is never wasted. From the purely materialistic point of view scientific research is not a luxury; for the community it is probably the cheapest form of investment. In order, however, that the community may fully realise all that it owes to the advancement of science the channels of communication between research and the public mind have to be kept clear, maintained and widened.

The necessity of conducting research for its own sake rather than for any material gain accruing from it is emphasised by Sir Richard Gregory:

> Almost all the investigations upon which modern industry has been built would have been crushed at the outset if immediate practical value had determined what work should be undertaken. Science brings back new seeds from the regions it explores, and they seem to be nothing but trivial curiosities to the people who look for profit from research, yet from these seeds come the mighty trees under which civilised man has his tent, while from the fruit he gains comfort and riches.

It has long been realised in Germany that the cultivation of the scientific habit of mind is largely a question of education, and the last war has taught us that if we are to retain our position among our fellow nations, Government provision must be made for education along scientific lines and also for research. Pure science is the rock upon which industrial progress rests. Science has revolutionised all standards of life, and upon chemical science, more than any other branch, depends man's material well-being and comfort. Pasteur, the chemist who gave the world the germ theory of disease, said:

> In our century science is the soul of prosperity of nations and the living source of all progress. A few scientific discoveries and their application are what really lead us forward.

There is scarcely an article in use which does not owe its existence to the application of some chemical principle. The production of machinery depends upon the chemist's studies of iron, steel and other metals. Our buildings are made from bricks and cement prepared under the chemist's supervision. We are equally dependent on the chemist for the clothes that we wear; the coins with which we purchase the necessaries of life; the drugs that cure us of disease; the glass for our windows and mirrors; and the fertilisers for raising crops. We look to the chemist for pure food, for pottery, paper, artificial silk, and for the paints and varnishes for our houses. Chemistry has provided us with gas and fuel for illumination and heating, petrol for our cars, and explosives for the mining industries. It shows us how coal may be made to yield ammonia, coal-tar and coke; how dyes can be obtained from the black, evil-smelling coal-tar; how combs and billiard balls can be made from milk; and how fats can be converted into dynamite. The chemist supplies our womenfolk with their silk stockings, perfumes, cosmetics, jewellery and leather footwear. We depend on him for such varied articles as rubber, soda, soap, electric lamps and wireless valves, photographic plates and films, anæsthetics, antiseptics, building materials and a host of other commodities. In fact nearly everything that we use results directly or indirectly from the work of the chemist. By his agency, raw materials of little value in their original condition can be transformed into really useful products. Air and water, for example, occur everywhere, and from the economist's point of view they are valueless. But the chemist can convert these relatively worthless substances into two very important chemicals, namely nitric acid and ammonia, both of which are employed in the manufacture of explosives and fertilisers. In addition, nitric acid is used in the manufacture of artificial silk, dyes, drugs, films, lacquers, artificial leather and gas mantles.

The last war showed us that national supremacy depends upon chemical supremacy. In other words, the nation that is chemically pre-eminent controls trade in time of peace and possesses the most efficient means of destruction in time of war. Undoubtedly the war showed us the darker side of science, although it would be more correct to say that it showed us the darker side of human nature. War, in effect, is the inevitable result of the struggle of nations for the raw materials of the chemist; for the coal, oil and mineral wealth which constitute the basis of industrial power. In spite of all the blue books and reports of international committees on the cause of the last war, the determining factor was undoubtedly a struggle for coal and mineral wealth. Political events merely provided an excuse for the declaration of war. The war aims of the Allies found clear expression in the peace terms which demanded the handing over of the most important German ore and coal fields. Scientific research received much encouragement from Government quarters during the war. If only it were so encouraged and subsidised in times of peace our conditions of life would be considerably improved.

We live in an age of feverish development, consuming the fruits of mother earth without a thought for the morrow. We are using up the stores of nature without considering that some of them can never be replenished. Every ten years we use as much coal as constituted man's entire previous supply over a period of some 100,000 years. The waste that is being carried on in the name of civilisation does not seem to have attracted the attention of the "practical" business man. In America, the home of big business, pirating and money-lust have exercised greater destructive activity than elsewhere. National wealth may be of two kinds—material wealth and energy wealth. The material wealth which includes coal, minerals and petroleum, occurs only to a limited extent and has been formed during the past geological epochs; the energy wealth comes, directly or indirectly, from the sun, and although we cannot increase it we can use it as advantageously as possible. We know that at the present rate of consumption the world's coal supplies will be depleted in a thousand years. In order to bring about the transformation of materials the chemist uses up energy, and at present his principal source of energy is coal. When our coal supplies are exhausted, we must either relapse into the civilisation of two centuries ago, before science ministered to our comforts, or else find a new source of energy. We know, too, that the minerals from which we obtain the metals used in every-day life will be used up in a few hundred years. The petroleum situation is even worse, chiefly owing to the large consumption of petrol in the automobile industry. Many oilfields are being run dry, especially in America, and the situation has only been saved by the discovery of new wells in Mexico, Russia, Persia and Mesopotamia. Even these cannot last for long at the present rapid rate of consumption. The chemist has pointed out that we cannot draw on nature's storehouse without jeopardising the future, and upon him depends the material salvation of mankind. He has shown us how chemical transformations can be accomplished by using up the minimum amount of energy. He has shown us how we can utilise coal to the best advantage, and in conjunction with the engineer he is already considering the conversion of coal into electric power at the pit-mouth to avoid the loss of energy involved in its transport. The power of waterfalls is also being used as a source of energy, but, unlike coal, such sources of energy are not depleted by use. It is possible that the final solution of the energy problem may be found in the chemist's researches on the atom.

The horoscope of iron, as cast by the International Geological Congress of 1910, does not seem very favourable. Thousands of tons of this metal are allowed to rust yearly and are then thrown on the scrap heap. All the nations are competing to see who can extract the most iron from the earth, and make from it bridges, battleships, guns, tools and machinery, only to let it revert into the substance from which it was obtained —rust or iron oxide. The chemist has taught mankind to fight rust. He has shown us how to protect iron by coating it with other metals, such as zinc, tin, nickel and chromium, and he has also produced special iron alloys that do not rust. Much scrap iron is also recovered by means of the electric furnace (p. 113). Furthermore, the chemist has shown how it is possible to replace iron by aluminium alloys for constructional purposes, and by cement for our buildings. Aluminium, which can be obtained from clay if need be, is certainly the metal of the future.

If the foregoing observations on the future shortage of the treasures of nature appear unduly pessimistic, let us seek consolation in the words of Berthelot, one of the greatest of French chemists. He visualises a future full of promise:

> Whenever energy can be obtained economically we can begin to make all kinds of food, with carbon borrowed from carbonic acid, hydrogen taken from the water and oxygen and nitrogen drawn from the air. . . . The day will come when each person will carry for his nourishment his little nitrogenous tablet, his pat of fatty matter, his package of starch or sugar, his vial of aromatic spices suited to his personal taste; all manufactured economically and in unlimited quantities; all independent of irregular seasons, drought and rain, of the heat that withers the plant and the frost that blights the fruit; all free from pathogenic microbes, the origin of epidemics and the enemies of human life. On that day chemistry will have accomplished a world-wide revolution that cannot be estimated. There will no longer be hills covered with vineyards and fields filled with cattle. Man will gain in gentleness and morality because he will cease to live by the carnage and destruction of living creatures. . . . The earth will be covered with grass, flowers and woods, and in it the human race will dwell in the abundance and joy of the legendary age of gold—provided that a spiritual chemistry has been discovered that changes the nature of man as profoundly as our chemistry transforms material nature.

If we attempt to trace the origin of the chemist's art we are lost in the twilight of civilisation. Although chemistry as a science only dates back to the days of Robert Boyle (1627–1691) there is no doubt that certain chemical processes were performed in a crude fashion by early man. Primitive man must have given some thought to the properties and relationships of various types of matter, and although he was familiar with comparatively few materials, knowledge acquired by accident and effort was passed down so that his successors were able to convert naturally occurring materials into new materials. The *art* of chemistry, or the transformation of materials, was practised by the Egyptians, Chaldeans, Hindus and Chinese. The Chinese acquired such perfection in the manufacture of certain articles that we must credit them with a considerable knowledge of some sort of technical or applied chemistry, conducted however in an empirical or rule-of-thumb manner. Among the many minerals known to the ancients were those containing the oxides of iron, copper and manganese; galena (lead sulphide), cinnabar (mercury sulphide), malachite (copper carbonate), and many precious minerals such as amethyst, beryl, lapis lazuli and turquoise. One of the most important chemical processes practised in pre-historic times was the extraction of metals, including the mechanical separation of gold, the smelting of iron, and the preparation of copper and lead. Silver, tin, mercury, bronze and brass were worked 4000 B.C. We find both the Egyptians and the Phœnicians highly skilled in the manufacture of glass, pottery, and enamel ware. The early Egyptians prepared fermented beverages and were expert in the arts of dyeing and embalming. At first they used dyes of vegetable origin. Mummy clothes, five thousand years old, have been found dyed with indigo and madder-root extract. At a later period dyes of animal nature appeared, among them kermes, a dye extracted from the body of an insect, and Tyrian purple, the purple of the Roman emperors, formed by exposing the secretions of certain Mediterranean shell-fish to light (p. 261). This would appear to be an example of one of the earliest photo-chemical actions. The leather-work of the Egyptians indicates that they possessed some skill in the tanning and colouring of leather. A study of ancient papyri also suggests that the inhabitants of the Nile Valley had an extensive practical knowledge of drugs of vegetable origin.

Until the fifth century B.C. these ancient peoples showed no desire to investigate the *nature* of the chemical processes they performed. This is not surprising since the operations were carried out by craftsmen who did not come into contact with the philosophers of the day. A complete barrier existed between the practical and the theoretical, and until the theoretical speculations of the Greek philosophers fertilised the practical knowledge of the artisan, chemistry as a science made little headway. The earlier Greek theories were concerned with the origin of the universe and with the ultimate constitution of matter. An atomic theory, evolved by certain Greek thinkers between 500 B.C. and 300 B.C., introduced the idea of atoms into chemical change. According to this theory matter is composed of very small particles or atoms which cannot be split up or destroyed, and between these atoms an empty space exists. The theory further postulated that atoms of different substances are different in shape, size and weight, and are all in constant motion, and that substances differ in properties according to the nature, number and arrangement of the atoms composing them. Unfortunately the Greek philosophers disregarded the experimental or research side of science, and they even neglected accurate observation to such an extent that they elaborated fanciful theories having no relation to actual facts. Obscure generalisations took the place of careful observations, and instead of studying nature at first hand the philosophers drew hasty conclusions from a few scattered facts.

The Greek period is important because it marks the period when man first considered the problem of the structure of matter. Certain Greek philosophers believed that a particular universal principle or primitive matter formed the basis of all forms of matter. We now meet the idea that law and order, not chaos and chance, rule the universe. Heraclitus (sixth century B.C.), whilst retaining the conception of a universal principle, introduced the idea of motion. According to him all matter is in a state of flux; nature is undergoing incessant change, a view summed up in his now famous dictum παντα ῥεῖ (*panta rhei*). Aristotle (384–322 B.C.) supposed that all matter was composed of four simple bodies or elements, fire, air, earth and water, and to these he added a fifth, which appears in later writings as the *quintessence* and more or less corresponds to our modern *ether*. This primordial quintessence acted as the carrier of the four fundamental properties of matter, hotness, coldness, dryness, moistness, and the combination of these properties in pairs gave rise to the four elements—fire (hot and dry), air (hot and wet), earth (cold and dry) and water (cold and wet). Aristotle's elements were therefore certain fundamental properties or qualities of matter, and by the combination of these different qualities different types of matter were formed. Since Aristotle believed that all substances were derived from the same primordial quintessence by impressing upon it different properties or qualities, he also accepted the possibility of one form of matter being changed into another by altering the amounts of the elemental qualities.

The ancient Egyptians evolved no general laws from their observations, nor did they attempt to classify phenomena. The early Greeks on the contrary, created vague and speculative theories having no experimental basis, and in many cases incapable of verification. Eventually, however, after the Roman conquest of Greece and Egypt, the practical knowledge of the Egyptians became mingled with the theoretical speculations of the Greeks. It is supposed that the two streams of knowledge met in Alexandria at the beginning of the Christian era. The idea of the transmutation of metals, that is the conversion of base metals such as lead into gold, probably arose from the experiments of the Græco-Egyptian metal workers, who produced alloys resembling gold from cheaper metals. Although such alleged transformations were fraudulent, the idea of transmutation fitted in quite well with Aristotle's theory of matter and gave mental satisfaction to the philosophically minded as well as to the more materially minded and fraudulent craftsmen. It is remarkable that from the time of the Greeks until the seventeenth century very few additions were made to the theories dealing with the composition of matter. Indeed, the doctrines of Aristotle and the idea of transmutation dominated chemical thought for over a millennium and a half. For a thousand years at least chemistry was practically synonymous with gold-making.

After the rise of Islam in the seventh century A.D. the Arabs translated many Greek works on chemistry, and although they added little to the existing knowledge, they brought about the effective union of the Greek theory and Egyptian practice. They erected a definite system of chemistry in which experiment and theory were correlated. Several chemical words have an Arabic origin. The Arabs gave us the word *alchemy*, derived from the Arabic *al*, meaning *the*, and *chemia* (Χημία), a word of Greek origin. *Chemi* meant Egypt, and *chemeia* the Egyptian Art, or the Black Art, from *chemeia*, meaning black. In a decree issued by the Roman Emperor Diocletian (A.D. 292), *chemia* was identified with the art of making gold and silver. Among other chemical words of Arabic origin are *alcohol*, *alembic* (a kind of retort), *borax*, *alkali* and *aludel*. The Arabic chemists, who fostered practical chemistry by the systematic study of the properties of different substances, classed all bodies as animal, vegetable or mineral. Geber (A.D. 721–813) appears to have been one of the foremost chemists of this period. He was familiar with the processes of crystallisation, calcination, filtration, reduction, distillation, and also with sulphuric acid, sal ammoniac, white arsenic and calomel (mercurous chloride). Some of these he prepared in a pure state by sublimation. Geber considered that all metals were composed of sulphur and mercury in varying proportions. By mercury and sulphur Geber meant not the common substances, but hypothetical bodies to which common mercury and sulphur approximate. The mercury imparted metallic properties such as a lustre, fusibility and malleability, and the sulphur conferred the property of combustibility. According to his view the differences between metals were due to the different proportions of sulphur and mercury, and by altering the relative proportions of these, metals could be transmuted into one another. The chemistry of organic substances appears to have been an object of study among the Arabs. They used milk, wool, bone, brains, hair and plant extracts in their preparations. Geber was also acquainted with acetic acid (from vinegar) and citric acid (from lemons).

After the decline of Arab learning (about A.D. 1200) the study of chemistry, or alchemy as it was then termed, spread over Europe. During the Middle Ages chemistry was dominated by mediæval religion and mysticism, and by the doctrines of Aristotle and transmutation. From the thirteenth century until the seventeenth the main object of the alchemists appears to have been the preparation of the *philosopher's stone*, the *stone of wisdom*, that could turn base metals into unlimited quantities of gold. Unscrupulous rulers often appointed Court alchemists to transmute lead into gold, and if we are to believe their accounts their efforts were successful. They based their claims on colour changes, since they had no criteria of chemical purity. They knew that copper could be converted into a silvery substance by treatment with arsenic compounds, and that when treated with zinc carbonate it produced a metal having the appearance of gold. We now know that the substances produced were copper alloys containing arsenic and zinc respectively, one having the appearance of silver and the other of gold. To the superficial observer it would appear that copper was transformed into a more precious metal. In view of the frauds that occurred in effecting these supposed transmutations alchemy became associated with quacks and charlatans, and the air of secrecy that pervaded their writings smothered rather than fostered true knowledge. To-day a scientific discovery of any value is published in special journals with a world-wide circulation. The alchemist, thinking that his labours would lead to the discovery of the philosopher's stone, made his writings almost unintelligible to others lest his secret should get abroad.

Not only did the alchemists seek the philosopher's stone, but also the *elixir vitae*, the panacea for all human ills, which was reputed to cure disease and prolong life. In their quest for gold the alchemists discovered many new and important substances, including nitric and hydrochloric acids, and many salts and alkalies. They also obtained a knowledge of chemical processes and perfected apparatus and methods. The big chemical industries are now annually making thousands of tons of some of the substances discovered by the alchemists. To quote the words of Francis Bacon:

> Alchemy may be compared to the man who told his sons that he had left them gold buried somewhere in his vineyard; where they by digging found no gold, but by turning up the mould about the roots of the vines, procured a plentiful vintage.

Under the influence of Paracelsus (1493–1541) chemistry developed as the handmaid of medicine. The chief aim of chemistry during this period seems to have been the production and purification of drugs for medicinal purposes, and the investigation of their composition and action. During the sixteenth and seventeenth centuries chemistry became known as iatro-chemistry (from *iatros*, a physician). The iatro-chemists gradually accumulated a large number of chemical facts, and since their drugs were carefully purified for medicinal use, they slowly arrived at criteria of chemical purity and chemical individuality. Paracelsus himself prepared compounds of mercury and antimony. Libavius (1540–1616) discovered tin chloride and described a method for preparing sulphuric acid. Van Helmont (1577–1644), the father of pneumatic chemistry, worked on gases and discovered carbon dioxide and impure hydrogen. He also made diligent use of the balance, and verified the principle of the conservation of mass—matter is not created or destroyed in a chemical change. Francis de la Boë (1614–1672), known to the world as Sylvius, investigated the nature of salts, which he recognised as compounds formed from acids and alkalies, and performed experiments on respiration and combustion. The iatro-chemical period also saw the growth of applied chemistry under Agricola (1494–1555), Palissy (1510–1589) and Glauber (1604–1668). Agricola advanced the study of mineralogical and metallurgical chemistry; among his discoveries were the metal bismuth and the flame tests given by certain compounds. Palissy laid the foundations of ceramics. Glauber, whose name is perpetuated in the purgative sodium sulphate, made careful investigations on the chlorides of the metals, and applied his knowledge to the manufacture of nitre and glass. During this period many organic substances were discovered, among them the salts of acetic and tartaric acids, stearic acid (from fats), succinic acid (by distillation of amber), oxalic acid and benzoic acid.

Robert Boyle (1627–1691), one of the founders of the Royal Society, has been referred to by a humorist as "father of chemistry and brother of the Earl of Cork". He studied chemistry as a science, not as a means of making medicines or gold, and he insisted on a strict observance of scientific method. His aim was "to find out nature, to see into what principles things might be resolved, and of what they were compounded". He introduced analytical methods for testing the composition of substances, and it is to Boyle that we owe the use of indicators for the detection of acids and alkalies. Until his time no sound system of scientific theory based on experiment existed. By means of well planned experiments and clear thinking Boyle swept away the false doctrines of both alchemist and iatro-chemist. He purged science, and chemistry in particular, of Aristotle's teachings on the four elements, and he pointed out the necessity for clear definitions of scientific terms. In Boyle's *Sceptical Chymist* (1661) we read for the first time the differences between mixtures, elements and compounds. According to Boyle an element is a substance that cannot be split up into other substances.

For nearly a hundred years after Boyle's death chemists devoted much of their time to the study of combustion and related phenomena. Although we credit Antoine Laurent Lavoisier (1743–1794) with the modern oxygen theory of combustion it should be noted that he had many predecessors who came very near the truth. Leonardo da Vinci (1452–1519) the artist, anatomist, philosopher and man of science, discovered that air consists of two parts, one, which we now call oxygen, capable of supporting combustion and necessary for respiration, and another, now called nitrogen, which does not possess these properties. John Mayow (1645–1679), an English doctor, proved that nitre and air contain a common constituent —which he called *fire-air*—capable of supporting combustion. He considered that during respiration the *fire-air* in the lungs converted the dark venous blood into bright red arterial blood. Unfortunately Mayow was prevented from following up these observations by his early death at the age of thirty-four.

A theory of combustion known as the *phlogiston* theory was developed in the latter part of the seventeenth century and the early eighteenth century. According to this theory a hypothetical substance, phlogiston, escaped from burning substances; the more readily and completely combustible the substance, the more phlogiston it contained. Although this theory explained many facts in connection with combustion, one fact was fatal to its progress. When a substance burns the products formed weigh more than the original substance. This had been recognised by Boyle. According to the phlogiston theory something escaped into the air during combustion, and this implied of course that the substance remaining weighed less than the original body.

A scientific theory, besides correlating facts, often opens out fruitful lines of enquiry. It does not follow that a rejected hypothesis has been of no service. The phlogiston theory, abandoned towards the end of the eighteenth century, was not a worthless explanation of combustion. In fact a number of important discoveries were made during the period in which the phlogiston theory reached its zenith. Cavendish (1731–1810), elucidated the nature of air, water and nitric acid, and Scheele (1742–1786), the brilliant Swedish chemist who made more discoveries than any of his predecessors, discovered oxygen, chlorine, tungsten, glycerin, prussic acid, potassium permanganate, and a large number of organic acids.

Many new gases were discovered by Joseph Priestley and by Scheele, and improved methods for collecting, handling and studying gases were devised. Joseph Black demonstrated the precise difference between carbon dioxide and air, and he showed the true relationship between the former gas and chalk. The mere accumulation of facts, useful as it is for the advance of science, is not the sole factor in scientific progress. Theories and laws are needed to interpret and correlate the facts. The chemical discoveries of the eighteenth century were not linked together by quantitative laws, nor were they interpreted by a comprehensive theory. Modern chemistry begins with Lavoisier, a victim of the French Revolution, yet himself the author of a revolution in chemical thought. Towards the end of the century Lavoisier overthrew the phlogiston theory, and conclusively proved that combustion is a rapid chemical union of a substance with the oxygen of the air (1784). He showed that air consists mainly of two gases, only one of which is consumed during combustion and breathing, and to this gas he gave the name oxygen. The other gas he called *azote*, but this was subsequently changed to nitrogen. With the advent of Lavoisier a new era dawned in the history of chemistry. In his hands the chemical balance became an important instrument, and he realised the necessity for determining the proportions by weight of the substances entering into a chemical change. His very accurate work with the balance established one of the fundamental laws of chemistry, the law of conservation of matter. With Lavoisier's new oxygen theory of combustion there arose a new system of chemical nomenclature. Henceforth compounds received names to indicate their composition and systematic names and terms were introduced for chemical processes.

As we have seen, an atomic theory of matter was held by certain classical writers of the pre-Christian era. Their views, which had no experimental basis, had little influence on the development of chemistry, although they were never lost sight of. John Dalton (1766–1824) re-formulated the atomic theory in such a way that it could be tested experimentally (1807). The theory was valueless until the deductions from it could be tested experimentally, and until chemical phenomena and the laws of chemistry could be quantitatively explained or co-ordinated. It required the genius of Dalton to modify the atomic theory so that it could be made to explain a number of chemical laws which had become firmly established. Briefly stated, Dalton's postulates are as follows: (1) Matter consists of atoms which are indestructible, indivisible, and differ in their nature and properties. (2) Atoms of the same element are all alike in properties and have the same weight, but they differ in properties from the atoms of other elements. (3) The atoms of elements unite to form compounds. Dalton realised that the *absolute* weights of atoms are very small, and only concerned himself with the determination of their *relative* weights, taking the weight of the lightest atom, that of the gas hydrogen, as unity.

It is impossible to give here any detailed account of the development of chemistry during the nineteenth century, owing to the specialised nature of many of the discoveries. But it may be mentioned that Dalton's theory had a remarkable influence on the progress of chemistry during that period. Indeed, with Lavoisier's work, it formed the basis of modern chemistry, and although Dalton's theory is no longer accepted in its entirety, it suffices for certain practical purposes. The atomic theory, far from being abandoned, has been productive of much research during the last fifty years.

The nineteenth century saw the rise of organic chemistry, or, as it is sometimes termed, the chemistry of carbon compounds. Until the end of the seventeenth century chemists devoted themselves mainly to the study of substances occurring in the non-living or mineral world. During the eighteenth century, however, the substances occurring in plants and animals began to attract the attention of chemists, and owing to their association with living or *organised* matter they were termed *organic* substances to distinguish them from the "inorganic" substances derived from the mineral world. Chemists drew a sharp line of division between these two classes of substances, and they further maintained that organic substances were built up within the living organism by the operation of a special power termed *vital force*. Although Lavoisier showed that organic compounds are composed in the main of carbon, hydrogen, oxygen and nitrogen, it was generally accepted for many years later that whereas inorganic substances could be artificially prepared by the chemist in his laboratory, organic substances could only be produced within living organisms.

In 1828 Friedrich Wöhler, a German chemist who later became a professor of chemistry at Göttingen, wrote to his friend Berzelius; " I must tell you that I can make urea without the aid of kidneys or of any animal". Wöhler had in fact made urea, a waste product of the body that is secreted by the kidneys into the urine, by warming ammonium cyanate. At that time urea was only known as a product of living organisms; on the other hand ammonium cyanate was essentially a laboratory creation. The production of a typical compound, urea, normally produced by the living organism, from inert or non-living matter was a preliminary to the bridging of the gulf that had seemed to separate the compounds of the inorganic world from those produced by the agency of living creatures. It is sometimes said that Wöhler's synthesis swept away the idea of vital force at one blow; this view is incorrect, because ammonium cyanate was obtained from animals' horns, hoofs and blood. The solution of the problem of synthesising organic substances from purely inorganic ones was slow, although it was stimulated by Wöhler's work. The idea of vital force was only gradually abandoned; it died a lingering death.

Wöhler's synthesis of urea remained the only one of note for many years. But by the middle of the century it was shown that numerous other substances, hitherto obtainable from living matter only, could be built up in the laboratory from simple inorganic compounds. It was further shown that organic substances obey the same laws of composition as inorganic substances. Although even to-day all substances that occur in the living organism have not been synthesised, a sufficient number of syntheses have been performed to show that the chemical transformations occurring in the living organism obey the same laws as those occurring in the laboratory. This does not mean that life can be explained solely in terms of chemistry. No organic compound as such ever shows the slightest sign of life.

For the purposes of classification it has been found convenient to retain the distinction between organic and inorganic chemistry, although to-day the term organic chemistry is restricted to the chemistry of the compounds of the element carbon. These now number over 230,000; the combined number of compounds of all the other elements is about 25,000. Among the organic compounds we include not only those formerly regarded as organic, that is compounds derived from the living organism, but also the compounds of carbon synthesised in the laboratory. By striking an electric arc between carbon poles in hydrogen, the gas acetylene is formed, and the treatment of this with water under suitable conditions yields another gas, acetaldehyde, from which alcohol and acetic acid—the acid in vinegar—may be obtained. From these two compounds numerous others can be prepared, and in this way an almost indefinite number of carbon compounds can be built up starting from the elements carbon and hydrogen.

Organic chemistry plays an important role in industry. We depend upon the organic chemist to produce antiseptics, drugs, explosives and perfumes from coal-tar; to convert cotton and wood into paper, artificial silk, explosives, photographic films and celluloid; and to prepare leather, soap, sugar, paints and varnishes, synthetic plastics and resins, rubber, and linoleum. A knowledge of organic chemistry is required to understand the changes that go on in the making of jam, the baking of bread, and the brewing of beer. Organic chemistry also helps us to follow the chemical processes that go on in our body, both in a state of health and disease.

CHAPTER II

THE ATOM AND BEYOND

We have seen that the early Greek philosophers evolved a simple atomic theory to explain the physical and chemical changes with which they were acquainted. This theory suffered an eclipse during the Middle Ages owing to the influence of Aristotle, the Greek thinker whose views were accepted almost in entirety by the mediæval chemists. Aristotle opposed the idea that matter is composed of atoms; he considered that it is continuous, that it is capable of being infinitely sub-divided. In other words, if a piece of silver were cut into small pieces and one of these pieces cut into still smaller pieces, and so on, the process could be repeated again and again indefinitely. According to the atomic conception of matter the process of division can be carried on only up to a certain point; it cannot be continued for ever. A point is reached when the particles of silver cannot be split up any further, even assuming that the eye were sufficiently keen and instruments were available for the purpose. These particles are called atoms. During the seventeenth century unsuccessful attempts were made by Sir Isaac Newton and Robert Boyle to revive the atomic conception of matter. Newton remarked:

> It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, movable particles, of such size and figures, with such other properties, and in such proportion to space, as most conduced to the end for which He formed them . . . those primitive particles, being solids, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces.

Note that Newton regarded atoms as hard and impenetrable —something like ivory billiard balls. To-day we regard the atom as rather like a very light pudding with currants in it, or to make the analogy more perfect still, like currants embedded in an imaginary pudding. In place of the pudding there is just empty space.

Chemists had no use for an atomic theory before the eighteenth century because until then they did not realise the importance of performing experiments quantitatively, that is, of weighing and measuring the substances undergoing change. Not until the time of John Dalton (1766–1844) did the atom assume a position of importance in the theory and practice of chemistry. Dalton first published his theory of the atom in the now famous work *A New System of Chemical Philosophy* (1808). In this he put forward the view that while the atoms of the same element are all alike in their properties, including mass, they differ from the atoms of other elements. The earlier atomic theories were vague and incapable of being tested. Dalton developed a theory that could be tested experimentally and that explained quantitatively the laws of chemical combination. According to the philosophers of antiquity all atoms consisted of the same primordial material; they only differed in their size and shape. Dalton's atoms differed in their properties and mass. Dalton also supposed that compounds result from the combination of small whole numbers of atoms of different elements, and that the "compound atoms"—which we call molecules—of the same compound are alike in all respects. These postulates supplied a ready explanation of the first fundamental law of chemistry, the law of constant proportions: the same compound always consists of the same elements in a constant proportion by weight. For example, common salt or sodium chloride is made up of the elements sodium and chlorine in the ratio of 23 to 35·5 by weight. Dalton explained this in the following manner. Let us suppose, he argued, that all elements representing the simplest types of matter are made up of infinitely small particles or atoms. Let us further suppose that the atoms of the same element are alike in weight, and that the ratio between the weight of a sodium atom and that of a chlorine atom is 23 to 35·5. According to Dalton the smallest particles which can enter into chemical combination are atoms. If one atom of sodium combines with one atom of chlorine—the simplest possible case of combination—the product will contain sodium and chlorine in the ration 23 to 35·5 by weight. If millions and millions of sodium atoms and the same number of chlorine atoms are involved, analysis of sodium chloride must still give the proportions 23 to 35·5. Dalton discovered a large number of the combining weights of elements using this principle. His rule that the atom is the smallest unit of matter than can take part in a chemical reaction still passes unchallenged. But Dalton took into account only the changes going on *between* atoms. He did not realise that there are changes going on *within* the atom.

Dalton's assumption that atoms combine in small whole numbers is capable of explaining another fundamental law of chemistry. Suppose two elements, A and B, unite so that one atom of A unites with one atom of B to form one compound. Let us further suppose that A and B form another compound by the union of one atom of A with two atoms of B. Then the weight of B in the two compounds will be in the ratio of the number of atoms of B present in each molecule—in this example 1 : 2. Here we have an explanation of the law of multiple proportions.

To-day we reserve the term atom for the ultimate particles of elements. Dalton failed to distinguish between the smallest particle of an element and the smallest particle of a compound. He termed the latter a "compound atom". It is obvious that the smallest particle of a compound must be composed of at least two atoms; a compound must consist of at least two elements, and there must be at least one atom of each element in the smallest particle of the compound. The smallest particle of a compound can still be divided up, since we can split it up into the atoms of the elements composing it. Since the word atom means indivisible it is not correct to apply it to the smallest particle of a compound. A new name is obviously required for this. In 1811 Avogadro, an Italian physicist, supplied it. He called the smallest particle of a compound, a molecule. An atom is the smallest particle of an element that can exist in a molecule, or stated in other words the smallest particle of an element that can take part in a chemical change. A molecule is the smallest particle of an element or compound that can exist in the free state. It does not follow that atoms and molecules of an element are identical. In most cases they are not. As a general rule the atoms of elements, especially of gaseous elements, do not go about singly, they associate in pairs, and each group of two atoms behaves as a distinct unit. Each pair forms a molecule, and for this reason we write the molecule of oxygen as O_2, hydrogen as H_2, nitrogen as N_2, and so on.[1] The atoms of argon, helium and those of the metals prefer to wander about alone; the atoms and molecules of such elements are identical. On the other hand the molecules of some elements consist of four (phosphorus) or even six (sulphur) atoms combined together.

According to Dalton the atoms of every element have a definite weight or mass. Although we cannot weigh atoms directly, we can find out how many times one kind of atom is heavier than another; that is we can find their relative weights. Since hydrogen is the lightest element known it is taken as a standard for comparison, and the number of times a given atom is heavier than an atom of hydrogen is called its atomic weight. It has been found more convenient to take the atomic weight of hydrogen as 1·008 rather than as 1. Then many of the atomic weights are approximately whole numbers.

From a study of gases and vapours we are forced to believe in the discontinuity of matter. We are compelled to imagine gases and vapours as a collection of minute particles or mole-

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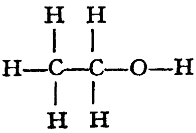
[1] It has been found convenient to use symbols to represent atoms and molecules. To each element a symbol is given, usually the first or the first two letters of the English name, or in the case of some metals the Latin name. The molecule of a compound can be represented by a formula, in which the small whole numbers below each symbol show how many atoms of the element are present. Thus $H_2 SO_4$ is the formula for a molecule of sulphuric acid, consisting of two atoms of hydrogen, one atom of sulphur and four atoms of oxygen. If we wish to represent the way in which the atoms of a molecule are combined together we write a *structural* or constitutional formula. The formula for alcohol is $C_2 H_6 O$, but this tells us nothing of the way in which the carbon, hydrogen and oxygen atoms are arranged. The following formula does :



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & & & \\ & & | & & | & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H} \\ & & | & & | & & & & \\ & & \mathrm{H} & & \mathrm{H} & & & & \end{array}$$

The lines or bonds connecting the atoms show how they are linked together.

cules that can crowd together or spread apart according to the conditions. If we increase the pressure on a gas its volume is diminished. How can compression of a gas diminish the volume of matter if this be continuous? If we suppose that matter is discontinuous, or that it is made up of very minute particles with spaces in between—like currants in a pudding—the compression suffered by the gas can be explained by the closer packing of the particles and the consequent diminution of the space between them. When the pressure on a gas is diminished the volume becomes greater. We explain this by assuming that the molecules spread apart, the space between them becoming greater so that they occupy a larger volume. This molecular theory also serves to explain why substances diffuse into one another. Coal gas will diffuse into air, sugar into water, and even gold into lead. The space between the molecules of one individual substance may be occupied by molecules of another substance. This theory further explains the three states of matter—solid, liquid, and gas. In a solid, which possesses rigidity, the molecules are nearly touching, and in the case of crystalline solids they are arranged in piles and rows. The molecules of a liquid are not so close and have more freedom, whilst those of a gas are spread very far apart. Bertrand Russell expresses this idea of the discontinuity of matter in the following words:

> To the eye or to the touch, ordinary matter appears to be continuous; our dinner-tables, or the chairs on which we sit, seem to present an unbroken surface. We think that if there were too many holes the chairs would not be safe to sit on. Science, however, compels us to accept a quite different conception of what we are pleased to call "solid" matter; it is, in fact, something much more like the Irishman's net, "a number of holes tied together with pieces of string". Only it would be necessary to imagine the strings cut away until only the knots were left.

We endow all molecules with perpetual motion, and the molecules of gases with the most rapid motion. The molecules of a gas travel in all directions with enormous velocity, and the pressure exerted by the gas is due to the molecules bombarding the walls of the vessel. As soon as the molecules collide with one another or with the walls of the vessel they rebound and resume their flight unceasingly with the same velocity. At any one moment the speed of an individual molecule may not be the same as that of its neighbour, but we can imagine an average speed for a particular kind of molecule. If we lower the temperature we can slow down the speed at which the molecules travel, and conversely a rise of temperature accelerates the speed. We know that the motion of the molecules in a substance is really its heat; the faster the molecules move the hotter the substance gets. At the "absolute zero", that is -273° Centigrade (523° F.) below the freezing point of water, all molecules are at rest and all gases then become solids.[1] It has been found possible to get within 1° C. of the absolute zero by rapidly evaporating liquid helium. Helium is a gas that occurs in minute quantities in the air.

It requires a little thought to realise how small molecules are, and with what an enormous velocity they move. No improvement can be made on Lord Kelvin's explanation of their comparative size:

> To form some conception of the degree of coarse-grainedness, imagine a globe of water or glass, as big as a football, to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion. The magnified structure would be more coarse-grained than a heap of small shot, but probably less coarse-grained than a heap of footballs.

One cubic inch of air contains something like 24×10^{13} or 240 trillion molecules, forty million of which would measure an inch if placed end on to one another. If all the molecules in a cubic inch of air were put in a row touching one another they would form a line 35,000,000 miles long, sufficient to go round the earth 1,400 times. Or, varying the analogy, if the atoms in a glass of water were thoroughly mixed with all the water in the world, and the glass filled with the mixture, it

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[1] The freezing point of water is 0° and the boiling 100° on the Centigrade (C) scale. On the Fahrenheit (F) scale these fixed points are 32° and 212° respectively. To convert one scale into the other the following expressions can be used:

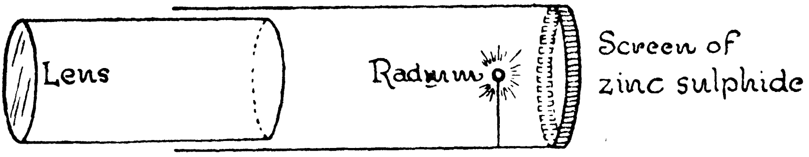
$$t°C = \frac{(t°F - 32)}{9} \times 5 \text{ and } t°F = \frac{t°C \times 9}{5} + 32$$

would still contain about two thousand of the original atoms. When the German paper mark fell to eight million per £1 sterling, one paper mark was still sufficient to purchase three billion gold atoms. Another illustration has been supplied by Johnstone Stoney. Imagine the volume of a pin's head magnified 10^{10} times (10,000,000,000); it would then be almost as large as the earth. Under similar circumstances molecules of air would be about 11 yards apart. Such figures really convey very little to the mind as they are far beyond the range of human comprehension. The best microscope will not reveal particles much smaller than $\frac{1}{60000}$ of an inch. The average speed of air molecules is about a quarter of a mile per second, or fifteen miles per minute. Even greater still are the speeds of the particles that form the framework of atoms and molecules—the electrons. These travel at one hundred and eighty thousand miles per second.

If only seeing constitutes believing we can never believe in the reality of atoms and molecules; the microscope at its best can only make visible objects thousands of times as large as an average sized molecule. No microscope can help us to see atoms and molecules, because light is a form of wave motion and light waves cannot reveal objects unless these are larger than the length of the wave. A new kind of light with a short wavelength is required in order to see atoms, and this new light has come to us in the form of X-rays. The discovery of radium and the X-rays has led to a revolution in our views on the structure of atoms and molecules.

Radium emits spontaneously three different types of penetrating rays, called α-, β-, and γ-rays. Any substance possessing the property of emitting these rays is said to be *radioactive*, and the property itself is called *radioactivity*. Baron Rutherford, Professor of Experimental Physics at Cambridge University, has shown that α-rays consist of positively charged helium atoms thrown off from radioactive bodies with a velocity approaching 20,000 miles per second, and their objective reality has been demonstrated without a doubt by Wilson, Professor of Natural Philosophy at Cambridge University. He allowed the α-particles given off by a small fragment of radium to enter a vessel of air saturated with moisture, and he then cooled the air. The α-particles broke up the air molecules into *ions*, or electrically charged particles, and these charged particles acted as condensation nuclei for the moisture, just as particles of dust act as nuclei for the condensation of water droplets to form a fog in a dirty atmosphere. The result is that fog settles along the tracks of the α-particles, and these fog tracks can be photographed with suitable illumination, appearing as bright lines against a blackened background. (*Plate* 5.) The traces form straight lines, or nearly straight lines lasting for a few seconds, after which they gradually disperse. The trains of droplets that suddenly appear like shooting stars offer us a tangible proof of the existence of isolated helium atoms. Each droplet is the result of a collision between α-particles, that is, charged helium atoms, and water vapour molecules.,

The production of α-particles from radium can also be shown by means of the *spinthariscope* (Fig. 1), a small instrument invented by Sir William Crookes. A minute speck of radium is fixed on a piece of wire supported inside a small metal tube just above a screen coated with zinc sulphide. If the screen is viewed in the dark through a magnifying lens, bright flashes of light appear, the effect resembling that of a swarm of fireflies on a dark night. Each flash is caused by an α-particle bombarding a zinc sulphide molecule, and by counting the number of flashes we can calculate the number of α-particles given off by a definite weight of radium in a given time.



The Spinthariscope

FIG. 1

How can a helium atom, which is much lighter than air and water vapour molecules, charge straight through these? This undoubtedly happens in the fog track experiment. There is only one explanation of this remarkable fact. There must be empty spaces in every atom; the space occupied by an atom cannot be completely filled with mass. The charged helium atom or α-particle, must *go through* the molecules it meets; it is impossible to assume that it goes round them. This means that we can no longer believe in the hard, round, impenetrable atoms postulated by Dalton. When air molecules collide in the ordinary way they recoil and resume their flight but in a different direction; when a charged helium atom, travelling at an enormous velocity, collides with another atom it goes through it. We can find a satisfactory explanation of this if we imagine that atoms have a structure like a solar system. The nucleus is the sun, and round it revolve the electrons which correspond to the planets. The nucleus has a positive charge of electricity, and each electron has a negative charge. Obviously the charge on the nucleus must balance the sum of the negative charge on the electrons so that the atom as a whole may remain electrically neutral. When a helium atom collides with other atoms it can pass through them just as one solar system might pass through another without the planets or suns colliding.

In 1827 Brown, a Scottish botanist, examined suspensions of pollen grains in water under a microscope, and he noted that the grains instead of being at rest darted hither and thither in an irregular fashion along zig-zag paths. All solids suspended in a liquid exhibit this phenomenon provided they do not exceed a size of about $\frac{1}{3000}$ of a millimetre. The explanation of this movement, now known as the Brownian movement, remained a mystery for many years. We know that it results from the incessant bombardment of the suspended matter by the molecules of the liquid. Let us imagine a large particle suspended in a liquid. It receives millions of blows on all sides from the molecules of the liquid, and the impacts produced on one side neutralise those on the other, with the result that the particle suffers little or no displacement. But when the particle is very small, at a particular moment it may receive more blows on one side than on the other, and so move in a definite direction. If it is sufficiently small, it will move first in one direction and then in another as a result of successive molecular impacts. This oscillatory motion of particles suspended in a liquid is really a manifestation of the motion of the liquid molecules; it is a magnified picture of molecular motion. The study of the Brownian movement has in fact provided the most convincing evidence for the real existence of molecules and for the perpetual molecular motion postulated by the kinetic theory of matter. Perrin, professor of physics at the Sorbonne in Paris, has actually calculated the size of molecules from a study of the Brownian movement of gamboge particles.

Perrin demonstrated in several ways that grains of the pigment gamboge behave exactly like ordinary molecules when suspended in a liquid. In a column of gas, the molecules are crowded together more closely at the bottom than at the top, as a result of the combined action of gravity and the spontaneous movement of the molecules. As the distance from the bottom increases in arithmetical progression the number of molecules in a given volume decreases in geometrical progression. Perrin found that particles of gamboge suspended in water not only obey this rule but behave in accordance with the laws which have been deduced for ordinary molecules. Since the suspended particles are visible, and can be counted, we ought to be able to calculate the number of individual molecules in one gram-molecule (molecular weight[1] expressed in grams) of a substance. This number, which is the same for every substance, is known as the *Avogadro number*. Perrin used gamboge particles of varying size suspended in water and other liquids, but he obtained the same value for the Avogadro number, namely $6{\cdot}06 \times 10^{23}$ molecules. This corresponds to $2{\cdot}705 \times 10^{19}$ molecules per cubic centimetre. These results compare favourably with those of Rutherford, who, by counting the number of helium atoms emitted by a given weight of radium and ascertaining the volume of helium, arrived at the value $2{\cdot}75 \times 10^{19}$ molecules per cubic centimetre. Whether the Avogadro number be calculated from the Brownian movement, from the physical behaviour of gases, from radio-activity measurements, or, most remarkable of all methods, from the blue colour of the sky, similar results are obtained. Such an array of facts must convince the most incredulous that atoms and molecules really do exist.

Much fresh light has been thrown on the structure of matter by a study of the effects of the electric discharge through highly rarefied gases. In 1859, Plücker discovered that an electric discharge passed through a glass tube containing a highly rarefied gas produces a blue glow, which passes from the cathode, or negative electrode,[1] to the other end of the tube. Here the glow induces a greenish kind of phosphorescence in the glass of the tube. Under ordinary conditions gases are non-conductors of electricity, but at very low pressures they permit the passage of an electric discharge, and at pressures in the region of ·01 of a millimetre a discontinuous glow fills the tube. The radiation emitted from the cathode, known as the cathode rays, travels in straight lines; the rays are characterised by the fluorescent effects they produce on the walls of the glass tube, and by the sharp and clearly defined shadows that they are capable of casting. If a concave cathode be used the cathode rays can be brought to a focus and will then raise metals to incandescence or even melt them. Sir William Crookes, who made an extensive study of the cathode rays, suggested that they consisted of minute negatively electrified particles and Sir J. J. Thomson, of the Cavendish Laboratory at Cambridge, has proved this. By very careful experiments he has measured the mass of these particles, the magnitude of the charge they carry, and their velocity. They travel at a velocity of from 10,000 to 100,000 miles per second, and have a mass equal to about $\frac{1}{1845}$ of that of the hydrogen atom or 9×10^{-28} gram (i.e. 9 divided by 10 twenty-eight times). This means that 90,000,000,000,000,000,000,000,000 cathode particles would weigh a gram. Such a colossal number cannot be conceived by the human mind. Even if the particles could be counted at the rate of five a second it would take all the people in the world nine hundred thousand million years to count them.

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[1] The molecular weight of an element or compound is the number of times its molecule is heavier than the *atom* (not molecule) of hydrogen.

The negatively charged particles constituting the cathode stream are called electrons. It is supposed that the electron is the unit of negative electricity, since a charge smaller than that carried by the electron has never been detected. The properties of an electron do not depend on the nature of the gas in the discharge tube or upon the nature of the cathode. Electrons can be emitted by all the known gases, by red-hot metals, by the action of ultra-violet rays upon metal surfaces, and by the filaments of a wireless valve. Radium and radioactive substances emit electrons, in which case they are called β–rays. Whatever their source the electrons are the same, and they therefore appear to be *common constituents of all atoms.* Atoms are no longer the fundamental units of matter. We now know that they are comparatively complex structures built up from units of negative and positive electricity. We no longer regard the atom as a hard impenetrable particle like an ivory billiard ball, but rather as a miniature solar system, in which the planets are electrons. Exactly the same electron is detected in the different elements and hence in the different kinds of atoms.

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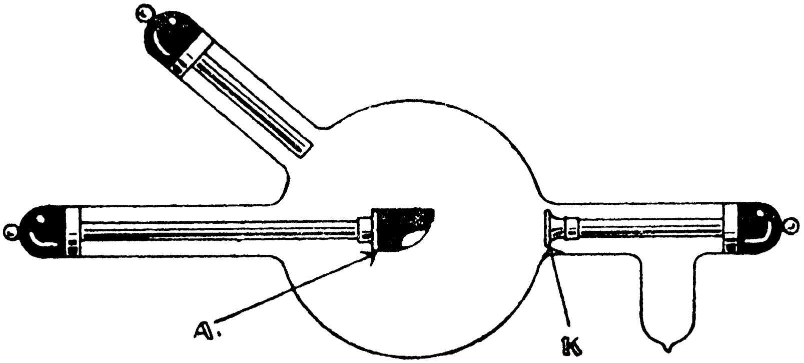
[1] The electrodes are the metallic wires or plates leading the electric current through the apparatus. The positive electrode is called the anode, the negative the cathode.



X-RAY TUBE

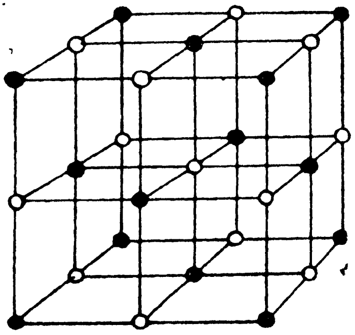
Electrons or Cathode Rays projected from Cathode K are focussed on Anti-Cathode A and produce X-Rays.

FIG. 2

In elucidating the mystery of matter we have a powerful weapon in the form of the X-rays. They were discovered in 1895 by Röntgen, who showed that exceedingly penetrating rays are produced when the cathode rays are focussed and allowed to fall upon an anti-cathode or target of dense metal (Fig. 2). These rays, called X-rays by Röntgen, are like light vibrations and wireless waves; they are vibrations in the ether. Yet they differ from light vibrations in that they have much smaller wavelengths. The rate of vibration of the X-rays is about

10,000 times more rapid than that of ordinary light waves. Furthermore, the rate of vibration of the X-rays depends upon the substance of which the anti-cathode or target is composed. It is a remarkable fact that every element is capable of emitting X-rays of a definite wavelength under certain conditions. If we allow X-rays of a short wavelength to bombard the substance this will emit its own characteristic radiation. Ordinary sunlight, or white light, consists of vibrations of very small wavelengths, and if passed through a prism it is split up into light of various wavelengths, which forms a spectrum. The colours of the visible spectrum are red, orange, yellow, green, blue, indigo and violet. At the violet end of the spectrum the wavelength is about $\frac{1}{60000}$ of an inch. This analysis of light can also be achieved by allowing the light to fall upon a diffraction grating, which is formed by drawing a large number of fine equidistant parallel lines on a piece of glass. Gratings have been prepared with 50,000 lines to the inch. Light which falls on the grating is diffracted or bent out of its normal course, and the degree of bending is constant for light of a given wavelength. Ordinary light can thus be analysed or sorted out into a spectrum with the aid of a diffraction grating.

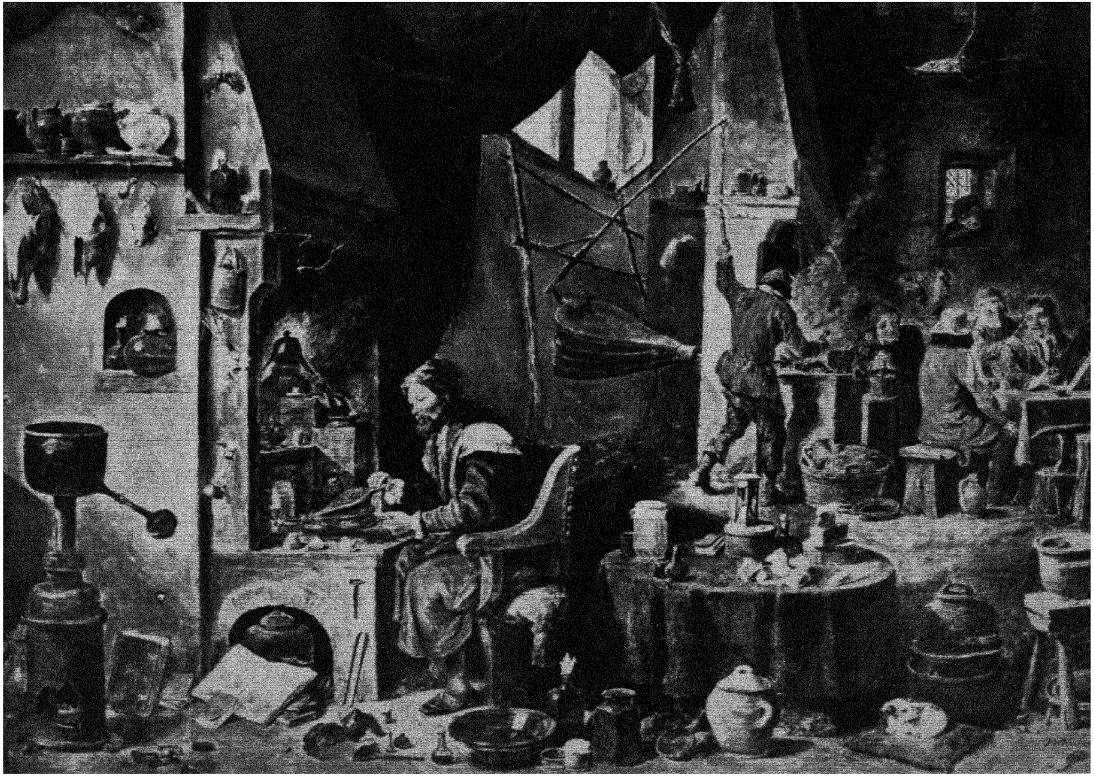
But an ordinary diffraction grating will not cause the X-rays to be bent out of their normal course, because their wavelengths are thousands of times smaller than those of ordinary light. It has long been considered that the atoms in crystals must be arranged in some particular and definite way, and in 1912 von Laue, of Zürich, suggested that the atoms of crystals might serve as the lines of diffraction gratings for the study of X-ray spectra. We cannot see atoms and molecules because they are much smaller than the wavelength of ordinary light, but the X-rays, the wavelengths of which are not much greater than the diameters of atoms, can detect their presence. Von Laue discovered that crystals supply us with natural diffraction gratings. The atoms composing them are arranged in rows, separated by distances roughly equal to the wavelength of the X-rays. When these rays fall on a crystal they are diffracted or bent just as ordinary light rays are bent by a diffraction grating. Laue directed a fine beam of X-rays through a thin slice or lamella of a crystal, and allowed the rays to fall upon a photographic plate. Tiny spots, caused through the scattering of the X-rays by the atoms in the crystal, appeared on the plate, arranged in a symmetrical fashion. A typical photograph of "Laue's spots" is seen on Plate 4. Each spot corresponds to the scattering of the X-rays by a plane in the crystal, and by comparing several photographs we can draw space models representing the relative positions of atoms in different crystals. W. H. and W. L. Bragg have studied in great detail the spatial arrangements of atoms in crystals by X-ray methods. They have shown that the crystals of common salt (sodium chloride) are cubic in form and that the unit cube is composed of electrically charged sodium and chlorine atoms or *ions*, arranged in the manner shown in Fig. 3, in which the white dots are sodium atoms and the black ones chlorine atoms. There are no molecules of sodium chloride as such in the crystal, but only atoms of sodium and chlorine built up into a cubical lattice, or mass produced pattern repeated over and over again. When atoms combine they do not lose their identities; chemical combination is merely an orderly atomic rearrangement.



Arrangement of atoms
in the crystal of
SODIUM CHLORIDE.
○·Sodium ●·Chlorine

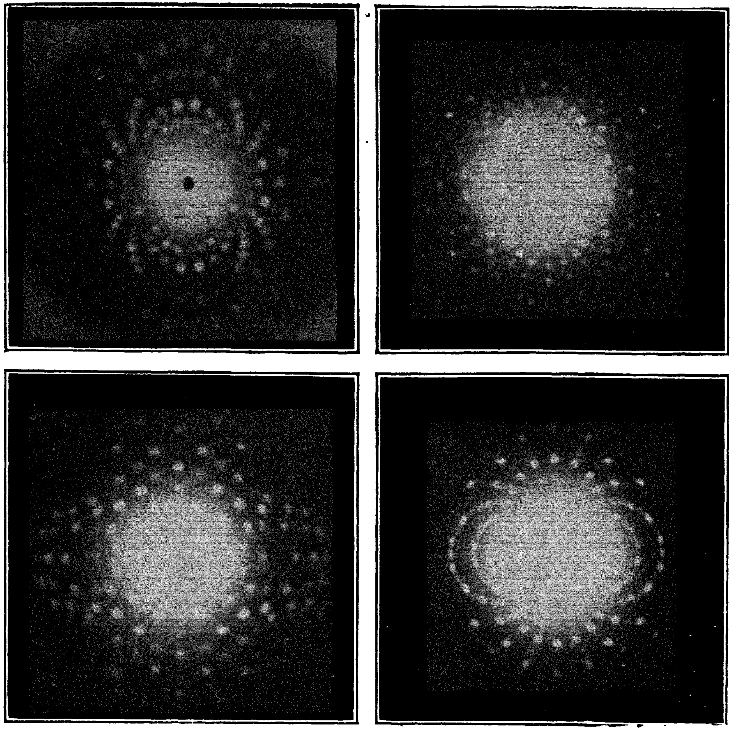
FIG. 3

The structure of the diamond crystal has also been



[By courtesy of *Deutsches* **Museum, Munich**

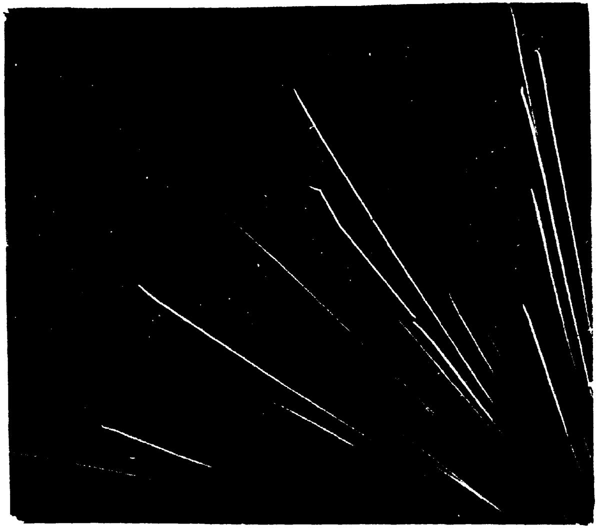
Plate 3.—THE ALCHEMIST'S LABORATORY, BY TENIERS



[*From "At Home Among the Atoms," by courtesy of the Century Co.*

Plate 4.—TYPICAL "LAUE SPOTS"

These are produced by passing a fine beam of X-rays through a thin film of a crystal and then allowing the rays to fall on a photographic plate. A symmetrical pattern made up of small spots is obtained. Each one corresponds to the scattering of the X-rays by a row of atoms in the crystal, and from the positions of the spots it is possible to deduce the structure of the crystal. Crystals can be identified by their "spot photographs," almost as easily as criminals from their finger prints. (See p. 33.)

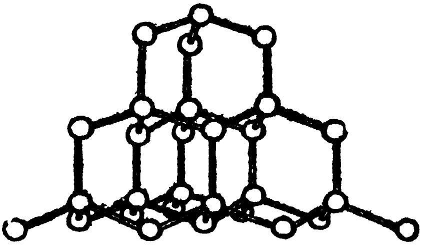


[*By courtesy of the Cambridge Instrument Co., Ltd.*,

Plate 5.—PHOTOGRAPHS OF TRACKS OF α–PARTICLES, by C. T. R. WILSON

These photographs prove that "solid" matter is mainly vacant space. The α-particles *pass through* the atoms in their path, knocking off an atom here and there. So many atoms become ionised that the paths appear continuous. The forks or sudden bends at the end of some of the tracks are due to α-particles passing so near the nuclei of atoms in their path that the particles are deflected. (See pp. 27, 36.)

elucidated by a study of its X-ray spectrum. It consists of atoms of carbon arranged in groups of six, forming a series of hexagons; each carbon atom is at the centre of the regular tetrahedron formed by the four atoms nearest it (Fig. 4).



Arrangement of carbon atoms in a diamond.

FIG. 4

For many years chemists have been puzzled over the way in which the carbon atoms are arranged in benzene, the molecule of which contains six carbon atoms and six hydrogen atoms (C_6H_6). Kekulé, a famous German chemist, suggested that the carbon atoms are united in a ring to form a hexagon, each carbon atom having attached to it a hydrogen atom. This was purely speculative, yet it has been strikingly confirmed by the X-ray examination of benzene. The benzene molecule has now been shown to have the shape of a regular hexagon, of side $6{\cdot}02 \times 10^{-8}$ cm., and thickness $1{\cdot}19 \times 10^{-8}$ cm.

A study of the properties of the α-, β-, and γ-rays emitted by radium has thrown a flood of light on the structure of the atom. The α-rays are positively charged particles of atomic dimensions ejected with a velocity of about one-tenth that of light. Each particle carries a double positive charge (i.e. twice that carried by a charged hydrogen atom or hydrogen *ion*) and has an atomic weight of four. The β-rays are none other than electrons, or units of negative electricity, shot out at a velocity almost equal to that of light. The γ-rays are the same as X-rays, and are probably produced by the impact of the electrons of radium on matter. Since the atomic weight of radium is 226, the emission of an α-particle of atomic weight four should leave an atom of atomic weight 222. This has been found to be so. The residue is called *radon* or radium emanation, and this in turn splits up spontaneously into several other products. Radium is in fact the progenitor of something like ten descendants, the last of which is lead. The α-rays are helium atoms with a double positive charge, that is, they have lost two electrons. A loss of two negative units, or two electrons, being the same as a gain of two positive units $[-(-2)=+2]$. Rutherford discovered that on losing their positive charge by taking up two negative electrons they form ordinary helium atoms. The explanation of this emission of helium atoms and of electrons from radium was given by Rutherford and Soddy in 1902. According to them, atoms of radium and the radioactive elements are complex bodies slowly undergoing spontaneous disintegration into the atoms of other elements. Changes go on *within* these radioactive atoms, not *between* them, as in ordinary chemical changes. Moreover, the changes cannot be started or stopped at will ; they take place at the same rate 200° C. below zero as they do at a red heat.

There is universal agreement to-day that atoms are complex bodies with a nuclear structure. Bragg showed that the α-particles from radium can pass through thin sheets of solid substances, and he further proved that they pass *through the atoms* of solids in their path. To account for these results Rutherford assumed that the atom consists of a charged massive nucleus occupying very little space, and that in this nucleus nearly the whole of the mass of the atom resides. Surrounding the nucleus but at some distance from it are the electrons. They are equal in number to the positive charge on the nucleus, and their mass is very small. According to Rutherford they are arranged around the nucleus in concentric spheres. Such a scheme explains how an α-particle can pass *through* an atom. Occasionally it may go too near the nucleus, and since both the α-particle and the nucleus have positive charges, the α-particle is deflected. In the photograph of the fog tracks caused by α-particles (Plate 5), distinct forks can be seen on some of the tracks. Each fork is caused by an α-particle passing so close to the nucleus of one of the atoms of the air or water vapour in the fog track chamber, that it is deflected. From the angle of deflection the mass of the nucleus concerned can be deduced, and it is found to be practically the same as the mass of the whole atom. From this we conclude that the mass of the atom is localised in the nucleus. It was originally suggested by Lord Kelvin and later by Sir J. J. Thomson, that atoms consist of a mass of positive electricity with electrons here and there, like currants in a cake. Such a view has been abandoned in favour of the nuclear atom.

So far the nature of the positively charged nucleus has not been discussed. Since the atoms of radio-active elements discharge α-rays, or positively charged helium atoms, it would appear that these are units in the architecture of the atoms of radio-active elements, and since the mass of the helium atom is four times that of an atom of hydrogen it would seem that helium is built up from smaller structural units. All the evidence goes to prove that the unit is the positively charged hydrogen atom, or a hydrogen atom that has lost one electron—a loss of a negative unit or electron being the same as a gain of a positive unit. The positively charged nucleus of the hydrogen atom, or the unit of positive electricity, has been termed the *proton.* Curiously enough William Prout suggested as far back as 1815 that the atoms of all elements were aggregates of some primordial material, or protyle, which he identified with hydrogen. It is a well established fact that if the atomic weight of oxygen be represented by the number 16 and that of hydrogen by 1·008, instead of 1, then the atomic weights of all the other elements approximate to whole numbers. Although this may possibly be due to chance, Sir William Ramsay has calculated that the odds are billions to one against this being so. The most likely explanation is that the positively charged hydrogen nucleus, of which the mass is 1, is the unit in the structure of the different atoms.

If the hydrogen nucleus consists of a proton, the nuclei of other elements must be more complicated and consist of both protons and electrons. The positively charged nucleus is responsible for practically the entire mass of the atom and the external negatively charged electrons for the entire volume of the atom. It has been found that the diameter of the electron is only about $\frac{1}{40000}$ times that of the atom, and the diameter of the proton is even smaller still, being about $\frac{1}{1800}$ times that of the electron. The atom then is mainly empty space, with a few specks dotted here and there. The helium atom must have a nucleus containing four protons, since the mass of the helium atom is four times that of the hydrogen atom. A study of the α-particle from radioactive bodies has shown us that the helium nucleus carries not four positive charges but only two, so that two electrons must be present in the nucleus to balance two of the positive charges. The *excess* positive charges would then be two. Since the ordinary helium atom is electrically neutral, two electrons must surround the nucleus, like planets round the sun, to balance the two positive charges. All atoms are considered to consist of a positively charged nucleus, made up of protons and electrons, and surrounding the nucleus at a distance are electrons equal in number to the excess positive charge on the nucleus. It has been found, too, that the number of nuclear electrons in the atom is half the atomic weight of the element concerned, provided that it is a whole number. Thus oxygen, atomic weight 16, contains 8 electrons within the nucleus of its atom.

If the atoms of all the elements are built up from hydrogen nuclei, and if these have a mass of 1·008, the atomic weights of the elements should be multiples of this or in most cases nearly whole numbers. They are approximately whole numbers in many cases, but several elements exist with fractional atomic weights. Chlorine is a case in point (35·457). In 1914 Theodore Richards, of Harvard University, found that the atomic weight of lead associated with the ores of uranium, a radioactive element, is 206·65; that of ordinary lead is 207·2. Frederick Soddy also found that lead derived from the decomposition of thorium, another radioactive element, might have an atomic weight of 208·4. Yet all these forms of lead were identical chemically. Soddy termed them *isotopes*. It gradually became clear that the atomic weight is not a fixed and fundamental characteristic of atoms at all, an assumption that had been accepted since Dalton's day. What is the fundamental characteristic? It is the *atomic number*. Suppose we arrange the chemical elements—ninety-two in number—horizontally in rows of eight in the order of their atomic weights, starting from hydrogen, which is allotted a place on its own. We then obtain a series as shown below, the numbers indicating the order of the elements.

							Hydrogen 1
Helium 2	Lithium 3	Beryllium 4	Boron 5	Carbon 6	Nitrogen 7	Oxygen 8	Fluorine 9
Neon 10	Sodium 11	Magnesium 12	Aluminium 13	Silicon 14	Phosphorus 15	Sulphur 16	Chlorine 17
Argon 18	Potassium 19	Calcium 20	Scandium 21	Titanium 22	Vanadium 23	Chromium 24	Manganese 25
. . .	up to 92						

This is the so-called Periodic Table of the chemical elements. (*See Plate* 9.) The number indicating the position of the element in the table is called its atomic number. This has been found to be equal to the excess of positive charges over negative charges in the nucleus of the atom, or equal to the number of the planetary electrons around the nucleus. Since the chief physical and chemical properties depend upon the planetary or outer electrons a knowledge of the atomic number is important.

In 1914 Moseley, a brilliant young physicist whose career was ended by a Turkish bullet at Gallipoli, devised a method for finding the atomic numbers of elements. His researches were based upon the discovery of Barkla and Kaye that each element, when bombarded by cathode rays in a vacuum tube, emits X-rays of a definite wavelength. Moseley passed these X-rays through a crystal, photographed the spectrum obtained, and from a study of the spectra arrived at the wavelengths of the X-rays. He found that different elements give different X-ray spectra and hence X-rays of different wavelengths. Two distinct types of rays are given off, known as the K and L series, each series being made up of a strong line (α-line) and a weaker one (β-line) close to it. Moseley found that if we know the number of vibrations per second of the α-line we can calculate the atomic number of the element giving off the X-rays.[1] This discovery enabled chemists to call the roll of the chemical elements for the first time, and to determine how many elements there are and how many are missing. The mass of the atom as indicated by its atomic weight is only of secondary importance; its properties are determined by its atomic number.

Since the electrons have a very small mass, and since the proton has nearly the same mass as the hydrogen atom, the mass of an atom is nearly equal to the number of protons in the nucleus. This would account for the fact that the atomic weights of many of the elements are nearly whole numbers, although some elements deviate from this plan. Harkins, an American chemist, has explained this deviation quite satisfactorily. He points out that protons and electrons are packed together so tightly in the nucleus that the energy changes produced affect their mass, and consequently the mass of all atoms, except that of the hydrogen atom, will be slightly altered by this *packing effect.*

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[1] It may interest the more mathematically minded that Moseley's expression was $V=\frac{3}{4}(N-1)^2\times C$, where C is a constant, V is the frequency of the α-line and N the atomic number. The frequency is the number of vibrations per second.

We have referred to chemically indistinguishable elements with different atomic weights. These isotopes, as they are called, all have the same atomic number, i.e. they occupy the same position in the Periodic Table of the elements, and they

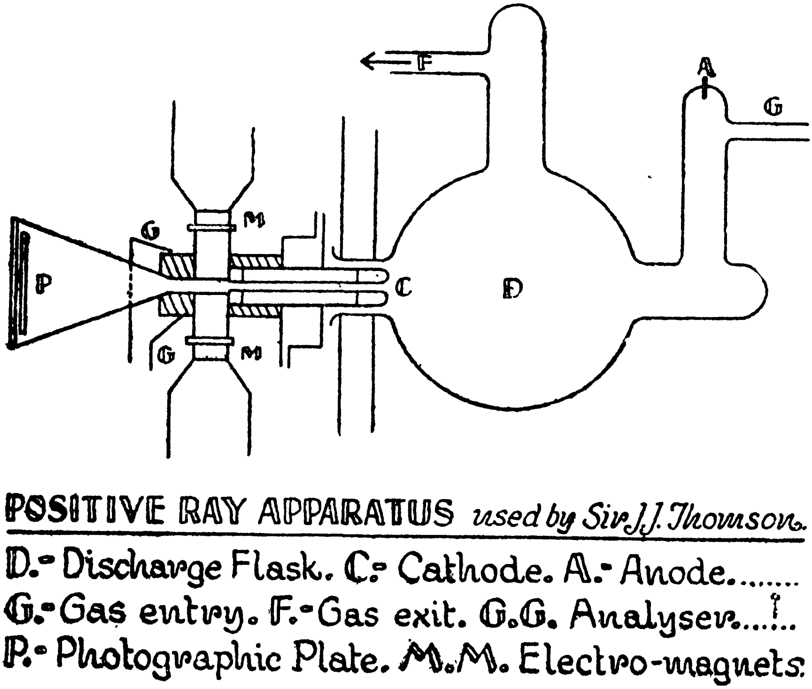

F
A
G
G
M
P
C
D
G
M
POSITIVE RAY APPARATUS used by Sir J.J. Thomson.
D.- Discharge Flask. C.- Cathode. A.- Anode........
G.- Gas entry. F.- Gas exit. G.G. Analyser....?..
P.- Photographic Plate. M.M. Electro-magnets.

FIG. 5

The gas to be examined passes into the flask D though the tube G. On passing the electric discharge between the electrodes, positively charged particles of the gas travel through the perforated cathode C. They pass on between the electro-magnets M M and strike the photographic plate P on which they record an electric spectrum. From this the mass of the particles can be deduced.

are identical in all their chemical properties. It has been recently demonstrated by Aston, of the Cavendish Laboratory at Cambridge, that many of the elements exhibit isotopy, that is, they are made up of atoms chemically identical, but differing in mass. Aston's apparatus, known as the *mass spectrograph,* is an improvement on that used by Sir J. J. Thomson in his *positive ray method* of gas analysis. If a perforated cathode be used in a vacuum tube for generating cathode rays, the rays pass through the perforations in a direction opposite to those of the cathode rays. Sir J. J. Thomson proved that these new rays, which are called *positive rays,* consist of positively charged atoms, or atoms that have lost an electron, and by subjecting the charged atoms to the influence of electric and magnetic forces he was able to sort them out and photograph them (Fig. 5). From the *electric spectrum* obtained he deduced the mass of the particles. Aston's method consists of sorting out the positive rays first through small slits S_1 and S_2 (Fig. 6) and then through two electrically charged plates P_1 and P_2, the positive rays being deflected towards the negative plate. The rays finally pass through a magnetic field, O, at right angles to the plates P_1 and P_2. Rays corresponding to particles of the same mass are brought to a focus at F on the photographic plate G B, where they are recorded as a definite line. If the rays are from an element consisting of a mixture of isotopes several lines are recorded on the photographic plate corresponding to the number of isotopes. From the position of the lines on the plate the mass of the atoms corresponding to them can be found. From Aston's experiments it would appear that ordinary chlorine is a mixture of atoms of mass 35 and 37 respectively, although the atomic weight as determined by

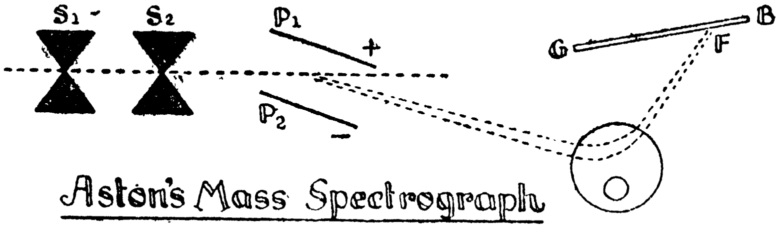


FIG. 6

ordinary chemical methods is 35·5. The isotopes of chlorine and mercury have recently been separated. Tin consists of about eleven isotopes. It was at first considered that the masses of isotopes were whole numbers, but in 1927 Aston, as a result of increased accuracy in his apparatus, detected slight deviations in the case of certain elements. Isotopes possess identical chemical properties because these depend upon the planetary or external electrons, and different isotopes of the same element possess the same number of external electrons. The nuclei of the isotopes differ in the number of protons present and this would account for the difference in mass; but it is to be noted that the nuclei have the same charge. From this it is clear that an element is a substance composed of atoms with the same atomic number or with the same electrical charge on the nucleus. An element may consist of a mixture of atoms differing in mass, yet chemically the atoms are identical.

We have previously pictured the atom as a kind of solar system, the satellite electrons revolving round the central nucleus. The simplest way of representing the hydrogen atom with an atomic number 1 would be:

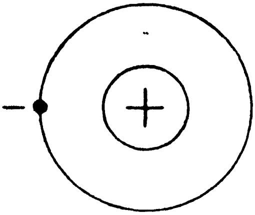


FIG. 7

and the helium atom with an atomic number of 2:

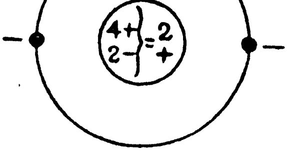


FIG. 8

The helium atom has a mass 4, and hence its nucleus must contain 4 protons and $4-2=2$ electrons. It has a charge of $+2$, and consequently there must be two electrons outside the nucleus to make the atom electrically neutral. According to Rutherford the planetary electrons revolve about the nucleus in rings, and it would appear that the maximum number of electrons in any ring is 8. When the number of electrons in the outer shell or ring is 8 we have a chemically inert atom. The atoms of the rare gases in the atmosphere—helium, neon, argon, krypton, xenon and radon are all chemically inert and with the exception of helium they have 8 electrons in the outer shell. The first shell surrounding the nucleus of the atoms of all elements, except hydrogen, consists of two electrons.

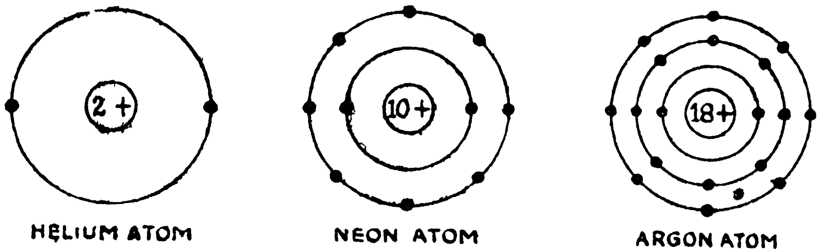


FIG. 9

Helium contains two electrons in its outer shell; neon has a shell of two electrons, and an outer shell of 8 (total 10). Argon has the same configuration as neon plus a further shell of 8 (total 18). Similarly krypton is divided into shells containing 2, 8, 8, 18 electrons (total 36). G. N. Lewis, an American chemist, suggested that the eight electrons in the shell occupied as their mean positions the eight corners of an imaginary cube, so that the successive atoms of elements from hydrogen onward are formed by the addition of protons and electrons to the nuclei. Helium has two electrons, and lithium (Fig. 10), the next element on the roll, commences with a new shell containing only one electron, the atom of each successive

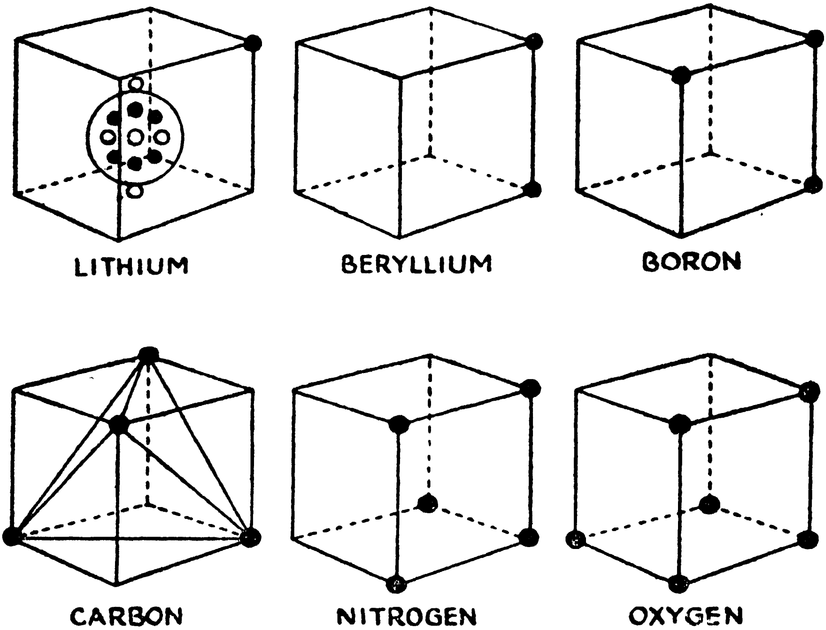


FIG. 10

element containing an extra electron in the shell until we come to neon, which is chemically just like helium. The structure of the atoms with an atomic number greater than that of neon is similar, and when the shell of eight electrons is completed another shell is formed, containing initially one electron.

The electron is at the heart of all chemical reactions; a chemical change involves the re-arrangement or transference of electrons. In chemical changes only the electrons external to the nucleus are affected; the latter is never touched. But a change in radio-active bodies such as radium involves a disturbance in the nucleus. In the case of the elements sodium and chlorine, which combine to form sodium chloride or common salt, we see that since sodium has an atomic number of 11, its atom must have one shell containing 2 electrons like helium, then another shell of 8, and a third shell with only 1 electron. Atoms with less than 8 electrons in the outer shell tend either to lose these outer electrons or to gain electrons until 8 are present in the outer shell. Chlorine has an atomic number of 17, hence the successive shells around the nucleus must contain respectively 2, 8, and 7 electrons. The chlorine atom thus tends to lose 7 electrons or gain 1 in order to have 8 electrons in its outer shell. When a sodium atom combines with a chlorine atom 1 electron is transferred from the sodium atom to the chlorine atom, thereby producing two systems with 8 electrons in the outer shell.

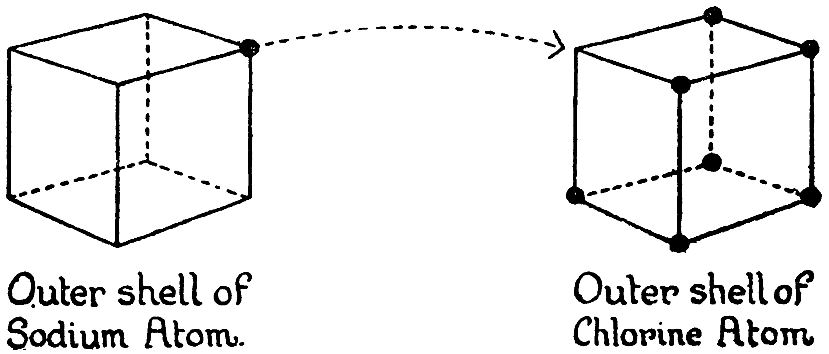

Outer shell of Sodium Atom.
Outer shell of Chlorine Atom

FIG. 11

Similarly hydrogen and oxygen combine to form water. Oxygen has 6 electrons in the outer shell, and hydrogen only 1. Since an oxygen atom desires 2 electrons to complete its outer shell of 8 electrons it must therefore combine with two hydrogen atoms, each of which supplies 1 electron. We may represent this by the following:

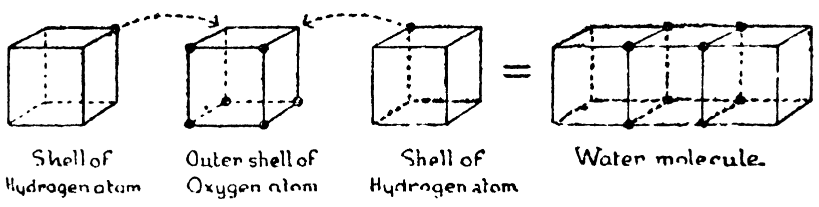

Shell of Hydrogen atom
Outer shell of Oxygen atom
Shell of Hydrogen atom
Water molecule.

FIG. 12

The cube or octet theory being essentially chemical, made no appeal to the physicists and mathematicians. As mathematicians pointed out, a system of electrons stuck at the corners of a cube does not constitute a stable system, and they further proved that the atom as we have described it could not exist according to the accepted theory of electro-dynamics. Niels Bohr, a Danish physicist, put forward a theory that has satisfied both the physicists and chemists. He assumes that the exterior electrons of an atom are in rapid motion about the nucleus, each electron travelling in a regular orbit, the complexity of which increases with the number of electrons. The orbits are not necessarily circular in all cases; elliptical orbits may be described around the nucleus as a focus. But according to the laws of classical dynamics a negatively charged electron revolving about a positively charged nucleus should radiate energy, and the orbit should get smaller and smaller until the electron is drawn into the nucleus. To overcome the difficulty Bohr assumes that under suitable conditions an electron can jump from one orbit to another with the absorption of a definite amount of energy termed a *quantum.*

The German physicist, Max Planck, applied the atomic theory to the study of energy problems. He concluded that energy, like matter, is not continuous, but is evolved or absorbed in a series of discontinuous "jerks" or finite packets of energy, or in units or atoms of energy, just as matter exists in atoms. We cannot have less than an atom of copper. In the same way we cannot have less than a unit, or *quantum* of radiant energy. The quantum is not a fixed quantity of energy; it varies with the frequency. If ϵ is the energy associated with a quantum and n is the frequency of the radiation, then

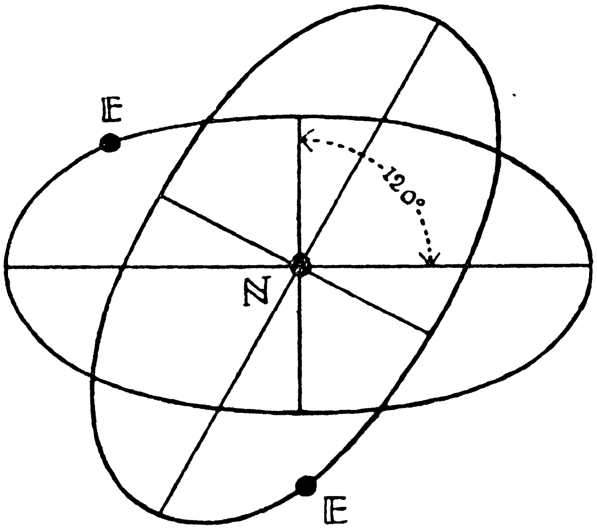
$$\epsilon = hn$$

in which h is known as Planck's constant or Planck's quantum. It is so small that one unit of it is involved in one revolution of the electron in its minimum orbit round the hydrogen nucleus. By accepting the quantum theory Bohr was able to show how an electron could describe a circle or an ellipse round the nucleus without radiating any energy. He imagines a number of ellipses of different sizes enclosing the nucleus, which serves as their common focus. The single electron moves along any one of these ellipses, but along one only. It may, however, jump from one ellipse to another, and in doing so radiates energy in the shape of light-waves. When an atom absorbs light instead of emitting it the energy taken up by the atom causes the electron to jump to a larger orbit. As long as an electron keeps to its own orbit it is not radiating energy, but if an external force acts upon it the electron jumps directly into another orbit with the liberation of energy of a definite wave length, and the amount of energy emitted is a quantum. The amount of energy associated with the quantum depends upon the frequency of the radiation emitted by the electron in its jump. This frequency multiplied by the quantity called Planck's constant equals the total energy radiated by the electron in passing from one orbit to another.

Bohr suggested that the electron always moves round the hydrogen nucleus in a circle, and that the most stable condition is obtained when the electron moves in a circle with a radius of $\frac{1}{20000000}$ of a centimetre. If it does not move in this circle it jumps into one with a radius four times as large, and if in turn it jumps from this circle into a larger one, this can only have a radius nine times that of the original circle. Bohr has proved mathematically that the only circles the hydrogen electron can travel in are those with radii 4, 9, 16, 25, 36 . . . times as large as the original. When the hydrogen electron jumps from one circle into a smaller one it emits light, and this will be one of the lines in the hydrogen spectrum, the actual line depending upon the particular jump made by the electron. It has been found experimentally by Balmer that the frequencies corresponding to a certain group of lines in the hydrogen spectrum can be represented by multiplying a certain constant figure—$109{,}737 \times 10^{-5}$cm. known as Rydberg's constant—by the quantity $(\frac{1}{4}-\frac{1}{n^2})$ where *n* may be 3, 4, 5, 6, 7. Two other series of lines can be obtained by multiplying Rydberg's constant by the expressions $(\frac{1}{9}-\frac{1}{n^2})$ and $(\frac{1}{1}-\frac{1}{n^2})$ respectively, where *n* has the values 4, 5, 6, etc., in the first expression and 2, 3, 4, in the second. The frequencies can be calculated by means of Bohr's theory. The frequency of the hydrogen lines obtained from Balmer's formula above is equal to Rydberg's constant multiplied by the difference between these two quantities. Now Bohr has shown that these two quantities in Balmer's formula correspond to the energies possessed by an electron before and after its jump from one orbit to another. Bohr was in fact able to deduce

Balmer's formula and also the value of Rydberg's constant. When the hydrogen electron jumps from a circle of radius 4 to the smallest circle it emits the spectral line with a frequency $(\frac{1}{1}-\frac{1}{4})$, i.e. $\frac{3}{4}$ of Rydberg's constant. If it jumps from circle 9 to the smallest circle we get a line that is $(\frac{1}{1}-\frac{1}{9})$, i.e. $\frac{8}{9}$ of Rydberg's constant; if it jumps from circle 9 to 4 the line is $(\frac{1}{4}-\frac{1}{9})$, i.e. $\frac{5}{36}$ of Rydberg's constant. And so on. The explanation of the spectral lines of hydrogen affords a powerful argument in favour of Bohr's theory. Sommerfeld has shown that Bohr's theory fits the facts better if we assume that the electrons move in an ellipse.

In a similar manner the Bohr atom explains how the spectra of other elements are produced. When the outer electrons of the atom of any element revolve in their respective orbits the atom radiates no energy. But when an electron jumps from one orbit into a smaller orbit nearer the nucleus, the atom emits



The HELIUM ATOM

E.E. are electrons revolving in elliptical orbits, inclined at an angle of 120° around the nucleus N.

FIG. 13

energy in the form of visible light waves, which give rise to the spectral lines characteristic of the particular element.

Complications occur when we consider the helium atom in the light of Bohr's theory. The helium atom contains two electrons outside the nucleus, and gives rise to two different spectra. Bohr considers that these two spectra may be due to one of the electrons moving in two different ways. The two electrons may describe orbits of the same size, but inclined to one another at an angle, or they may move in different orbits round the nucleus. Each electronic arrangement gives a characteristic spectrum. The most stable form of the helium atom is supposed to consist of a nucleus around which two electrons move in similar orbits inclined at a plane of 120° (Fig. 13).

Enough has been said for the reader to realise what an intricate structure an atom really is. To quote the words of Jean Perrin, the French physicist:

> Atoms are no longer eternal, indivisible entities, setting a limit to the possible by their irreducible simplicity ; inconceivably minute though they be, we are beginning to see in them a vast host of new worlds. . . . Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and above all, unfathomably immense.

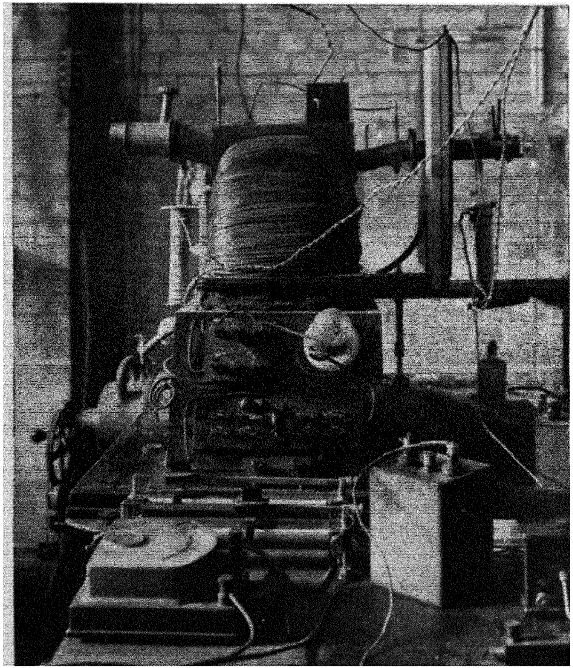
CHAPTER III

THE CHEMICAL ELEMENTS

The word element has had a variety of meanings both in ordinary and chemical usage. The definition that has long been current among chemists is due to Robert Boyle, who wrote in his *Sceptical Chymist* (1661):

> I mean by *elements*, as those chymists, that speak plainest, do by their principles, certain primitive and simple, or perfectly unmingled bodies; which, not being made of any other bodies, or of one another, are the ingredients of which all other substances are immediately compounded, and into which they are ultimately resolved.

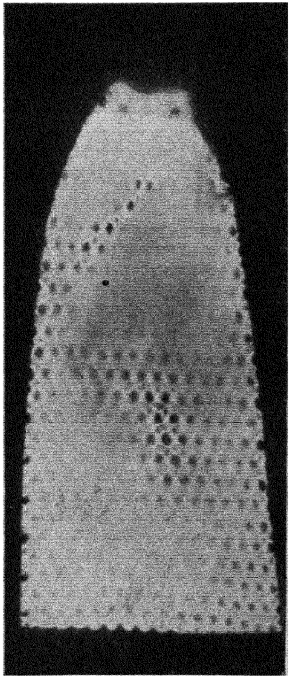
Plainly stated, Boyle considered that an element is a single substance that cannot be split up into anything simpler; it resists analysis; it consists of one kind of matter, and no physical or chemical process can extract from it more than one kind of substance. Air can be separated into at least two substances, oxygen and nitrogen. Water can be split up into oxygen and hydrogen by the passage of an electric current, and by a similar method common salt can be separated into two components, sodium and chlorine. But no chemist has succeeded in separating from oxygen anything but oxygen, or anything but hydrogen from hydrogen. Nobody has ever obtained anything else from sodium or chlorine, or from any of the common metals; and conversely it has also been found impossible to elaborate or synthesise these bodies from other substances. They are termed elements. It is quite possible that in the future, chemists may show that the substances now considered to be elements are not elements at all. In the past it has repeatedly happened that certain substances passed as elements; at a later date improved methods of analysis showed them to be mixtures or compounds of elements. Lime, magnesia and alumina were



[*By courtesy of Dr. Aston and the Royal Society*

Plate 6.—DR. ASTON'S MASS SPECTROGRAPH

This is the apparatus employed by Dr. Aston, of Cambridge, to show that many elements are a mixture of isotopes, that is they are made up of atoms chemically identical but differing in atomic weight. (See p. 41.)



[*By courtesy of the Lighting Trades, Ltd.*

Plate 7.—A GAS MANTLE PHOTOGRAPHED BY ITS OWN RADIOACTIVITY

The mantle was pressed flat on a photographic plate wrapped in black paper, and left for ten days to a fortnight. The above photograph was obtained on developing the plate and printing out. The image of the gas mantle was formed on the plate in the dark by the radioactive rays from the thorium contained in the mantle. (See Ch. IV.)

[*By courtesy of The Director of Publications H.M.S.O.*

Plate 8.—NEON LIGHT, CROYDON AERODROME (See p. 68.)

considered by Lavoisier to be elements because at that time they could not be resolved into anything simpler. We now know that these so-called elements of Lavoisier are not elements at all but compounds of oxygen with the elements calcium, magnesium and aluminium respectively.

Boyle's definition of an element given above fell upon barren ground. Until the epoch-making work of Lavoisier on combustion, some hundred and twenty years after, Boyle's teaching received little recognition. With the advent of Lavoisier's *Traité élémentaire de chimie* (1789) a new spirit was infused into the life of chemistry, and henceforth the analysis and classification of different types of matter became one of the main objects of the science. Boyle's definition, clear and logical as it was, could not be satisfactorily tested experimentally. Lavoisier supplied the modern conception of an element:

> If we apply the term element or principle to bodies to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all substances into which we are able to reduce bodies by decomposition. Not that we are entitled to affirm that these substances which we consider as simple, may not themselves be compounded of two, or even of a greater number of more simple principles; but since these principles cannot be separated, or rather, since we have not hitherto discovered the means of separating them, they are, with regard to us, as simple substances, and we ought never to suppose them compounded until experiment and observation have proved them to be so.

Lavoisier's classification of lime, magnesia and alumina as elements was perfectly logical, and he realised the possibility of their eventual decomposition into simpler substances when he wrote:

> We are certainly authorised to consider them simple bodies until by new discoveries their consitutent elements have been ascertained.

In other words, the term element is a purely conventional one, and it represents the accuracy obtainable by the most recent methods of analysis. Since Lavoisier's day the methods and technique of analysis have been so perfected that whereas Lavoisier knew of only 28 elements, we can now muster 90. Thirteen years after Lavoisier's death in 1794 Sir Humphry

Davy showed how electricity might be used to resolve some of the so-called elements. By passing an electric current through lime he clearly demonstrated that this substance can be resolved into oxygen and a metal, which he termed calcium, and he further showed that lime can be formed by the combination of calcium and oxygen. In a similar manner Davy resolved potash, soda, baryta and strontia into the elements potassium, sodium, barium and strontium respectively.[1] The greenish-yellow gas chlorine, discovered in 1774 by Scheele, was long considered to be a compound body containing oxygen until Davy pointed out in 1810 that it must be an element, since it could not be decomposed by any method then available. Time has confirmed Davy's statement; nobody has yet separated anything simpler from chlorine.

Ever since Lavoisier's day chemists have been attempting by every means at their disposal to decompose all available materials, and up to the present time the existence of some 90 different elements has been proved; it would appear that only two more remain to be discovered. But the problem is not quite as simple as it looks. Shortly after the discovery of the radioactive elements it was found that these substances are gradually disintegrating; they are constantly throwing off helium atoms and electrons by the gradual disruption of the nucleus. Radium, for example, slowly disintegrates to form lead. But the rate of these changes cannot be altered by any human agency. The rate at which they occur is the same at red heat as it is at the temperature of liquid air. This altered the definition of an element to a simple substance that cannot be resolved into or built up from anything simpler by *human agency*. But while this definition met the difficulty of radioactive changes, it did not satisfy chemists for long. In 1919 Sir Ernest Rutherford bombarded nitrogen atoms with α-particles, some of which hit the nucleus of the nitrogen atoms, which were broken down into hydrogen and helium. Bombardment of aluminium gave similar results; it lost an electron and was converted into hydrogen and an element of lower atomic weight.

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[1] Perhaps the reader has heard of Hilaire Belloc's lines:—

Sir Humphry Davy
Abominated gravy.
He lived in the odium
Of having discovered sodium.

THE CHEMICAL ELEMENTS.

Atomic Number		Symbol	Atomic weight	Atomic number		Symbol	Atomic weight
1.	Hydrogen	H	1·008	47.	Silver	Ag	107·88
2.	Helium	He	4·00	48.	Cadmium	Cd	112·40
3.	Lithium	Li	6·94	49.	Indium	In	114·8
4.	Beryllium	Be	9·02	50.	Tin	Sn	118·7
5.	Boron	B	10·83	51.	Antimony	Sb	121·76
6.	Carbon	C	12·004	52.	Tellurium	Te	127·5
7.	Nitrogen	N	14·008	53.	Iodine	I	126·93
8.	Oxygen	O	16·00	54.	Xenon	Xe	130·2
9.	Fluorine	F	19·00	55.	Caesium	Cs	132·81
10.	Neon	Ne	20·18	56.	Barium	Ba	137·36
11.	Sodium	Na	23·00	57.	Lanthanum	La	138·9
12.	Magnesium	Mg	24·30	58.	Cerium	Ce	140·2
13.	Aluminium	Al	26·97	59.	Praseodymium	Pr	140·9
14.	Silicon	Si	28·1	60.	Neodymium	Nd	144·3
15.	Phosphorus	P	30·98	61.	Illinium	Il	—
16.	Sulphur	S	32·06	62.	Samarium	Sa	150·4
17.	Chlorine	Cl	35·46	63.	Europium	Eu	152·0
18.	Argon	A	39·94	64.	Gadolinium	Gd	157·0
19.	Potassium	K	39·10	65.	Terbium	Tb	159·2
20.	Calcium	Ca	40·09	66.	Dysprosium	Dy	162·5
21.	Scandium	Sc	45·1	67.	Holmium	Ho	163·5
22.	Titanium	Ti	47·90	68.	Erbium	Er	167·6
23.	Vanadium	V	50·95	69.	Thulium	Tm	169·4
24.	Chromium	Cr	52·04	70.	Ytterbium	Yb	173·0
25.	Manganese	Mn	54·95	71.	Lutecium	Lu	175·0
26.	Iron	Fe	55·84	72.	Hafnium	Hf	178·6
27.	Cobalt	Co	58·95	73.	Tantalum	Ta	181·3
28.	Nickel	Ni	58·69	74.	Tungsten	W	184·1
29.	Copper	Cu	63·55	75.	Rhenium	Re	—
30.	Zinc	Zn	65·38	76.	Osmium	Os	191·0
31.	Gallium	Ga	69·72	77.	Iridium	Ir	193·0
32.	Germanium	Ge	72·60	78.	Platinum	Pt	195·2
33.	Arsenic	As	74·93	79.	Gold	Au	197·2
34.	Selenium	Se	79·2	80.	Mercury	Hg	200·6
35.	Bromine	Br	79·92	81.	Thallium	Tl	204·0
36.	Krypton	Kr	82·9	82.	Lead	Pb	207·2
37.	Rubidium	Rb	85·4	83.	Bismuth	Bi	209·0
38.	Strontium	Sr	87·63	84.	Polonium	Po	—
39.	Yttrium	Yt	88·93	85.	—	—	—
40.	Zirconium	Zr	91·2	86.	Niton (Radon)	Nt	222·0
41.	Niobium	Nb	93·3	87.	—	—	—
42.	Molybdenum	Mo	96·0	88.	Radium	Ra	225·95
43.	Masurium	Ma	—	89.	Actinium	Ac	—
44.	Ruthenium	Ru	101·7	90.	Thorium	Th	232·15
45.	Rhodium	Rh	102·9	91.	Protoactinium	Pa	—
46.	Palladium	Pd	106·7	92.	Uranium	U	238·2

This necessitated a further definition: Elements are substances which cannot be resolved into or built up from anything simpler by the ordinary types of chemical change. We must regard bombardment with α-rays as an extraordinary type of chemical change. From the chemist's point of view matter is resolvable or unresolvable; all substances are ultimately resolvable into certain types of elementary "stuff". But we do not regard elementary matter as being ultimately unresolvable as we have seen above and in the last chapter. For practical purposes, however, we may take it that no such resolution occurs during ordinary chemical changes.

When we speak of new chemical elements being "discovered" we really mean that some new element has been detected or isolated, which had previously escaped detection either because of its extreme rarity, or on account of its lack of easily recognised physical and chemical properties. It may occasionally happen that other matter associated with it masks its presence or renders its separation difficult.

On page 53 is a table of the known chemical elements with their atomic numbers, atomic weights and symbols. Most of these will be quite unfamiliar to the average reader. This is not surprising since only twelve elements form the bulk of the earth's crust, the atmosphere, and the water of the globe. The following figures, supplied by Clarke and Washington of the U.S.A Geological Survey, show the percentages of the twelve commonest elements.

Oxygen . .	50·02
Silicon . .	25·80
Aluminium . .	7·30
Iron . .	4·18
Calcium . .	3·22
Sodium . .	2·36
Potassium . .	2·28
Magnesium . .	2·08
Hydrogen . .	·95
Titanium . .	·43
Chlorine . .	·20
Carbon . .	·18
	99·00

From this we see that the first twelve elements account for about 99 per cent of the earth's surface. Very few of the elements occur free; they are chiefly combined with other elements in the form of compounds. Oxygen is the most abundant of the elements; this might be anticipated since one-fifth of the air, and eight-ninths of the water of the globe consist of oxygen. Silicon, which follows in order of abundance, is a constituent of sand, rocks and clay. The above figures give us no idea of the composition of the earth's interior. It is thought that beneath the crust of the earth, which consists largely of oxygen and silicon, there occur zones which get poorer in silicon and richer in iron. Molten iron and nickel are supposed to form the innermost core of the earth. Of the 8,000 miles of the earth's diameter 6,000 probably consist of highly condensed gaseous iron. An analysis of the spectrum of the sun's atmosphere has shown that most terrestrial elements also occur in the sun's atmosphere. An extremely light element termed *coronium*, unknown on earth, has been stated to occur in the sun's corona. *Asterium* and *nebulium* two other extremely light elements unknown on earth, have been stated to be present in nebulae and very hot stars.

The chemist tries to find out as much as he can about the elements; how they occur in nature; their extraction; their behaviour, especially with respect to one another, and above all their classification. He has found that the majority of the elements are not widely distributed upon the earth, and that very few are found in the free or native state. This is because the elements combine with one another to produce compounds. Indeed, the 90 elements are capable of forming some half a million compounds, and the element carbon is responsible for about half of these. In studying the properties of the elements and their compounds we classify them into two groups: metals and non-metals. A study of the chemical elements shows that some of them are very similar in their chemical properties, and they have accordingly been arranged in families or groups. The halogen family, for example, consists of fluorine, chlorine, bromine and iodine. They are all very reactive, combining readily with metals and also with hydrogen to form compounds having a similar composition to one another. Other families include the alkali family (lithium, sodium, potassium, rubidium and caesium), so called because the oxides of these elements form alkalies with water; the inert gases of the atmosphere (helium, neon, argon, krypton, xenon, radon); and the nitrogen family (nitrogen, phosphorus, arsenic, antimony and bismuth).

This grouping of elements into families was merely a preliminary to a more efficient means of classification. In 1863 J. A. R. Newlands observed that if the elements were arranged in the order of ascending atomic weights every eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music. In other words, if the elements be arranged horizontally in groups of eight the elements in the vertical columns possess similar properties. This relationship he termed the law of octaves.

Hydrogen	Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen
Fluorine	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphor
Chlorine	Potassium	Calcium	Chromium	Titanium	Manganese	Iron

The first three of Newlands' octaves are shown. Lithium, sodium and potassium share corresponding physical and chemical properties; they are bright silvery metals that tarnish in air, decompose water to form alkalies, and dissolve in acids. Similarly, beryllium, magnesium and calcium show a resemblance in their properties. Newlands was handicapped because several elements known to us were undiscovered in his day and his table occasionally failed to give the expected harmony. Thus according to his scheme manganese should have properties similar to those of phosphorus, whereas in actual practice there is no resemblance whatever. Like most innovators, Newlands received nothing but ridicule and hostile criticism for his work. One fellow chemist even went so far as to ask him if he had ever thought of arranging the elements according to their initial letters, and another wag suggested that there were new possibilities in the field of music with the law of octaves. Although the Chemical Society of London refused to publish Newlands' paper, the Royal Society awarded him the Davy Medal twenty-one years later.

De Chancourtois, who had also suggested a classification of the elements on the basis of their atomic weight in 1862, was less successful than Newlands. His observations failed to attract any attention. Only after his death, when the Periodic Classification of the elements was generally accepted, did his work receive any recognition.

Newlands' discovery led to further inventigations by a Russian chemist, Dmitri Ivanovitch Mendeléeff (1839–1907), a professor in the University of St. Petersburg. In 1869 he published his now famous *Periodic Classification* of the elements, a revised form of which is still in use. Mendeléeff, realising that Newlands' idea of octaves could not be applied to all the elements, suggested a new arrangement. Taking the first fourteen elements in the order of their atomic weights, he arranged them in two groups of seven, and these were followed by three groups of seventeen, each of which could be split up into three parts: one group of seven, a group of three, and another group of seven with properties resembling those of the first seven. Mendeléeff called each of the groups with seventeen in it a "Long series". His Periodic Classification, brought up to date, is given on Plate 9. It is based on the principle recognised by Mendeléeff, that "the properties of the elements and of their compounds are a periodic function of their atomic weights". This may mean nothing to the average reader, yet it contains the solution to nearly all the problems of chemistry, including the structure of the atom and the ultimate origin of the elements. It would be no exaggeration to state that the principles enunciated by Mendeléeff have been the most important guide in inorganic chemical research for the last sixty years.

A few words of explanation of the Periodic Table are necessary. The combining capacity of the atoms of the elements, or their *valency*[1] as it is called, increases as we pass from group to group. In Group I all the elements have a common valency of 1 and their chemical properties are very similar; lithium, potassium, rubidium and caesium, however, resemble one another more than they do copper, silver and gold—the latter three metals forming a sub-group. In Group II the common valency is 2. Beryllium and magnesium in the two short series resemble one another and so do calcium, strontium, barium and radium, the first elements of the three long series. Zinc, cadmium and mercury, the second elements of the long series also show striking resemblances. The same is true throughout the different groups each of which contains, as it were, two chemical families. Passing from group to group the valency increases up to a maximum of 8. In Group VIII there are three groups of what are termed transition elements. These split each long series into two groups of seven, and they consist in each case of three metals with almost identical properties, e.g. iron, nickel and cobalt.

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[1] Chemists have found that the atoms of a given element always combine with a definite number of atoms of another element. The atoms of the various elements thus have a certain combining capacity, or *combining value*, or *valency* as it is usually called. Any atom of oxygen combines with two atoms of hydrogen to form water; any atom of nitrogen will combine with three of hydrogen to form ammonia; any atom of chlorine combines with one of hydrogen to form hydrochloric acid. No element is known of such combining power that two or more atoms of the element are required to keep one atom of hydrogen in combination. Chemists have therefore taken the combining

In Mendeléeff's original table there was a large number of vacant spaces corresponding to elements unknown in his day. He predicted a series of elements after hydrogen in Series I with atomic weights 1·4, 1·8, 2·2, 2·6, 3·0 and 3·4. Y in the table is, according to Mendeléeff, an analogue of helium with an atomic weight of ·4. He supposed that it might be *coronium*, a hypothetical element in the sun's corona. X he called Newtonium, after Newton, with an atomic weight of ·000001. Mendeléeff supposed that this formed the luminiferous ether, although the existence of this is no longer assumed by modern physicists.

Mendeléeff insisted that any anomalies in the order of the elements in the table were not due to defects in his scheme, but to errors in the atomic weights. In many instances it was

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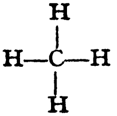
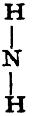
capacity or valency of hydrogen as the standard. The number of atoms of hydrogen with which one atom of an element will combine is termed the valency of the element. It follows that the valency must be a whole number. The union of elements is often represented graphically by drawing a number of bonds or lines corresponding to the valency, from one element to another, thus



$$H-\underset{\displaystyle \begin{matrix}|\\H\end{matrix}}{\overset{\displaystyle \begin{matrix}H\\|\end{matrix}}{C}}-H$$

METHANE,
a compound of
CARBON & HYDROGEN



$$\begin{matrix}H\\|\\N\\|\\H\end{matrix}$$

NITROGEN HYDRIDE,
or AMMONIA

H—O—H (Oxide of Hydrogen or Water).

proved that the atomic weights had been miscalculated, and ever since its introduction the Periodic Table has afforded an excellent, if not infallible, guide in correcting atomic weights. The atomic weight values for indium, beryllium and uranium were once under suspicion because these elements did not fit very well into the table. Mendeléeff's alteration of the supposed atomic weights to make these elements fit the table was subsequently justified by new atomic weight determinations. The system still suffers from many inperfections. Argon, with an atomic weight of 39·9, occurs before and not after potassium with an atomic weight of 39·1, whereas the contrary should hold good. Similarly tellurium (127·6) comes before iodine (126·9) in the table. But a study of the atomic numbers of these elements, deduced from their X-ray spectra, has confirmed this order.

The table of elements as published by Mendeléeff in 1869 contained only sixty-three recognised elements and he suggested that the vacant spaces in the table corresponded to elements that exist in nature, although methods of chemical analysis had failed to detect them. Mendeléeff had such faith in his scheme that he not only predicted the existence of several new elements, but also described in detail their physical and chemical properties and those of their compounds. In 1871, elements with atomic weights 44, 70 and 72 respectively were unknown and gaps existed in Mendeléeff's scheme corresponding to elements having these atomic weights. For example, a gap existed between silicon and tin, another between aluminium and indium and yet a third just below aluminium. Mendeléeff termed the hypothetical elements corresponding to these blanks eka-silicon, eka-aluminium and eka-boron respectively and he further predicted their properties in a remarkable manner. Rare minerals were examined and the whole realm of nature ransacked in search of new elements. Some four years later Lecoq de Boisbaudran discovered in a zinc ore of the Pyrenees a new element which he termed gallium, and this proved to be none other than Mendeléeff's eka-aluminium. In 1886 Clemens Winkler examined a silver ore known as argyrodite and detected in it a hitherto unknown element, to which he gave the name germanium. The properties of this element turned out to be identical with those prophesied by Mendeléeff for eka-silicon. The following table shows the accuracy of his predictions:

Property	*Eka-silicon*	*Germanium*
Atomic weight	72	72.5
Specific gravity	5.5	5.47
Colour	Dirty grey	Greyish-white
Actions of acids	Slight	Slight
Action of alkalis	Practically none	Practically none

A similar agreement in properties was found to exist between Mendeléeff's eka-boron and the metal scandium. This was discovered in a Scandinavian mineral by Nilson in 1879.

The position of hydrogen in the Periodic Table presents some difficulty. There is no room for it in Group I or Group VIII. Some have supposed that it is a member of a series of elements as yet undiscovered on earth, which includes the hypothetical *coronium*, *nebulium* and *protofluorine*. Rydberg, who conducted many observations on spectra, considered that these hypothetical elements come between hydrogen and helium in the Periodic Table. He claimed to have seen their spectra in the sun's corona, and although other investigators have confirmed this and have reported the presence of coronium in volcanic gases, the existence of these hypothetical elements on the earth is now doubted. Modern atomic theories can find no place for atoms lighter than those of hydrogen. The experiments on the scattering of X-rays by gases further suggest that hydrogen and helium occupy consecutive positions in the Table. Moreover, a green line seen in the spectrum of the sun's corona in 1869 and supposed to be caused by coronium, was scarcely observed during the eclipse of 1914. Instead a red line was seen. Modern spectroscopy has shown that certain spectral lines previously attributed to these hypothetical elements are really due to gaseous oxygen and nitrogen under low density conditions, such as prevail in certain nebulae. These lines attracted the attention of Huggins as far back as 1867. We know that the same gas can give different spectra, the actual spectrum obtained depending upon the pressure of the gas—and hence its density—and upon the strength of the electric discharge through the gas. It has been suggested that owing to the enormously high temperatures existing in some nebulae, the atoms of oxygen and nitrogen lose electrons and so give rise to spectra different from those that normally characterise these elements. According to Bohr's theory of the atom, spectra are produced when an electron or electrons jump from one orbit to another orbit nearer the nucleus.

The usefulness of Mendeléeff's Periodic Table cannot be over-estimated. It enables the elements to be classified according to their atomic weights and hence serves as a check upon doubtful atomic weight values; it has guided the search for new elements and it is undoubtedly related to much of the new knowledge of the structure of the atom. We have seen how an increase of atomic weight means an increase in the number of protons in the nucleus. It is the positive charge on the nucleus of the atom that determines the atomic number of an element; and the atomic number is its position in the Periodic Table. In the light of modern knowledge chemists now realise that this is a table of atoms rather than of elements.

The discovery of isotopes has not invalidated the Periodic Table. All the isotopes of an element occupy the same place in the table and therefore possess the same atomic number and the same X-ray spectrum. Aston's results show that each place in the Periodic Table may be occupied by a "simple" element, that is, one that forms no isotopes, or by two or more isotopes forming what was once considered a single element. It would certainly be incorrect to say that the Table has been abandoned in favour of modern atomic theories. On the contrary it forms the keystone of our knowledge on the structure of the atom.

The relationship between the classification of the elements and the structure of their atoms presents an interesting study. Suppose that we modify Mendeléeff's scheme and arrange the elements in successive columns in the order of their atomic numbers. According to our most recent knowledge only two more elements remain to be discovered. There are only two gaps in the series of the elements arranged according to their atomic numbers and these gaps correspond to: (1) a member of the chlorine or halogen family with an approximate atomic weight of 218 and an atomic number of 85, (2) a member of the sodium or alkali-metal family with an atomic weight of 224 and an atomic number of 87.[1] Our revised plan of the elements is given in the table below, only the symbols of the elements being given.

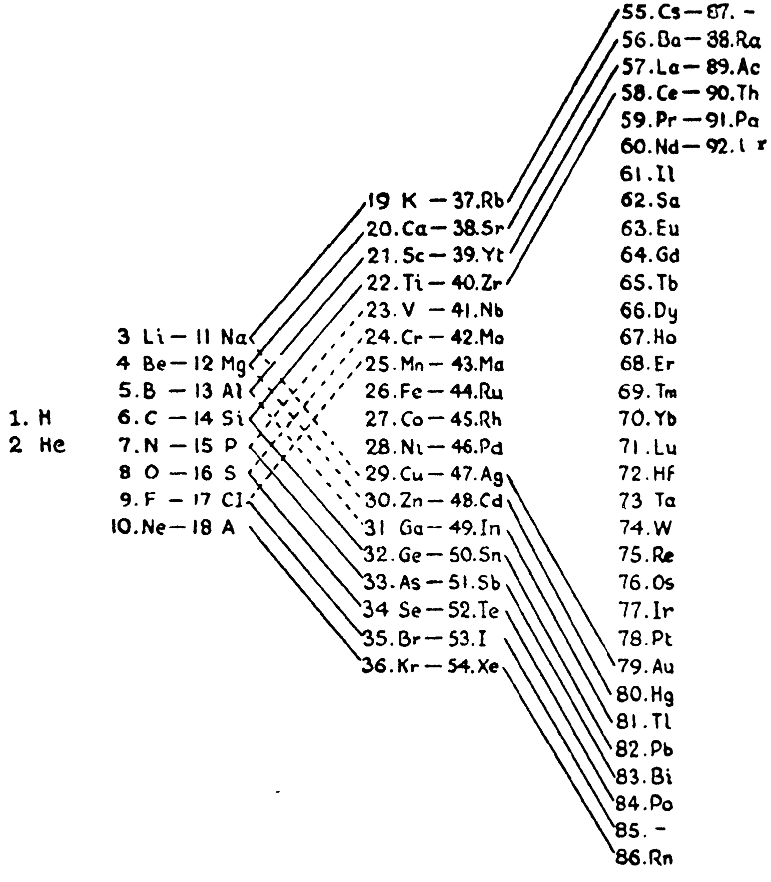

55.Cs—87. -
56.Ba—88.Ra
57.La—89.Ac
58.Ce—90.Th
59.Pr—91.Pa
60.Nd—92.U
61.Il
62.Sa
63.Eu
64.Gd
65.Tb
66.Dy
67.Ho
68.Er
69.Tm
70.Yb
71.Lu
72.Hf
73 Ta
74.W
75.Re
76.Os
77.Ir
78.Pt
79.Au
80.Hg
81.Tl
82.Pb
83.Bi
84.Po
85. -
86.Rn
19 K —37.Rb
20.Ca—38.Sr
21.Sc—39.Yt
22.Ti—40.Zr
23.V —41.Nb
24.Cr—42.Mo
25.Mn—43.Ma
26.Fe—44.Ru
27.Co—45.Rh
28.Ni—46.Pd
29.Cu—47.Ag
30.Zn—48.Cd
31 Ga—49.In
32.Ge—50.Sn
33.As—51.Sb
34 Se—52.Te
35.Br—53.I
36.Kr—54.Xe
3 Li—11 Na
4 Be—12 Mg
5.B —13 Al
6.C —14 Si
7.N —15 P
8 O —16 S
9.F —17 Cl
10.Ne—18 A
1. H
2 He
I
II
III
IV
V
VI
VII

FIG. 14

In column I are two elements; in column II eight; in column III eight; in Columns IV and V eighteen; in column VI thirty-two. Column VII contains only six. Neglecting column VII the numbers of elements in the columns can be written:

---

[1] Chemists at Cornell University, New York, now claim to have mapped the X-ray spectrum of element 87 (Nov. 1931).

$2 \times 1^2 = 2$ in column I
$2 \times 2^2 = 8$,, ,, II
$2 \times 2^2 = 8$,, ,, III
$2 \times 3^2 = 18$,, ,, IV
$2 \times 3^2 = 18$,, ,, V
$2 \times 4^2 = 32$,, ,, VI

The reader will note that each column terminates with a member of the rare gas family (helium, neon, argon, krypton, xenon, radon), the atomic numbers of which can be written:

$$2\,(1^2+2^2+2^2+3^2+3^2+4^2+\;\ldots\;)$$

Helium has an atomic number of	$2\,(1^2)$	$= 2$
Neon	$2\,(1^2+2^2)$	$= 10$
Argon	$2\,(1^2+2^2+2^2)$	$= 18$
Krypton	$2\,(1^2+2^2+2^2+3^2)$	$= 36$
Xenon	$2\,(1^2+2^2+2^2+3^2+3^2)$	$= 54$
Radon	$2\,(1^2+2^2+2^2+3^2+3^2+4^2)$	$= 86$

This mathematical series, too precise to be due to mere chance, is believed to be closely connected with atomic structure. According to Bohr, the planetary electrons of the atom can leave one orbit for another and in doing so radiate a definite amount of energy—a *quantum.* Return to the smallest orbit from the orbits of the highest "quantum numbers" causes the emission of ultra-violet rays and a jump from one orbit to another with the emission of smaller quanta produces visible rays. The maximum number of electrons in the atoms with orbits of different quantum class is:

Orbits of quantum number 1 hold 2 electrons.
Orbits of quantum number 2 hold 8 electrons.
Orbits of quantum number 3 hold 18 electrons.
Orbits of quantum number 4 hold 32 electrons.

These numbers are in the series 2×1^2; 2×2^2; 2×3^2; 2×4^2. That is, the maximum number of electrons of quantum number n is $2n^2$. As the rare gases are the last elements in the first six columns of Fig. 14 we can formulate a rule concerning the electronic arrangements of the atoms of the elements in each column or period.

Helium in Period I (Fig. 14) has 2 electrons outside the nucleus, each electron revolving in an orbit of its own. There is never room for more than one electron in the same orbit; this is a special application of what physicists call the "exclusion-principle." The atoms of the elements of Period II have orbits of quantum number I containing 2 electrons like helium, and in addition orbits of quantum number 2, holding from 1 to a maximum of 8 electrons. The atoms of the elements of Period III have three types of orbits—those of quantum number 1, 2 and 3—holding 2, 8 and from 1 to a maximum of 8 respectively. In Period IV there will be sets of 2, 8, 8 and from 1 to 18 orbits, each holding an electron. Period VI will contain elements whose atoms possess sets of 2, 8, 8, 18 and from 1 to 32 orbits and hence the same number of electrons. This law of uniform atomic plan discloses the inner meaning of the Periodic Law in terms of the arrangement of electrons within the atoms. By the careful use of the formula

$$N = 2\ (1+2^2+2^2+3^2+3^2+4^2+\ .\ \ .\ \ .)$$

where N = the atomic number, we can calculate the atomic numbers of elements if their positions relative to the inert gases in the Periodic Table are known. For example, barium is in Group II of the Table (Plate 9) and in the same Period (6) as the inert gas xenon, whose atomic number is $2\ (1+2^2+2^2+3^2+3^2)=54$. As xenon is in Zero Group and barium in Group II, the atomic number of barium is $54+2=56$. Referring to the Table again it will be seen that iron is in Group VIII and in the same Period (4) as the inert gas argon, whose atomic number is $2\ (1+2^2+2^2+3^2)=18$. Hence the atomic number of iron is $18+8=26$. It is most likely that in the text-books of the future atomic numbers and not atomic weights will figure as the fundamental property of elements.

The discovery of the rare gases of the atmosphere is a fascinating chapter in the history of chemistry. Although argon was not isolated until 1894, it narrowly escaped detection some hundred and ten years previously by Henry Cavendish, a recluse who interested himself in chemistry.[1] He passed electric sparks through air confined in a glass tube and absorbed the gases produced in a solution of an alkali. Cavendish stated that:

> Only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air[2] let up in the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest . . . we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.

Cavendish's observations were soon forgotten. Before 1894 only eight groups of elements found a place in the Periodic Table. In that year Sir William Ramsay[3] and Lord Rayleigh isolated a hitherto unknown gas from the air by repeating Cavendish's experiment with the advantage of modern apparatus. Lord Rayleigh was engaged at the time in determining the densities of gases and he observed that the density of nitrogen obtained from the air was greater than that of nitrogen prepared from compounds of the element. Sir William Ramsay suggested that the discrepancy might be due to a heavier gas in the air with properties similar to those of nitrogen. The two investigators joined forces and in a few months added another element to the list. They named it *argon* (from the Greek *argon*, idle), because it was exceptionally inert and obstinately refused to enter into combination with any known element or compound. It was also prepared by removing oxygen from the air with red-hot copper, drying the residual gas with soda-lime and

[1] Cavendish, '*le plus riche de tous les savants, et le plus savant de tous les riches*', was of a very retiring disposition and had many eccentric habits. Various stories have been told of these. On one very rare occasion he invited friends to dinner—very rare because he usually dined alone—and his housekeeper asked him, "What will you have for dinner to-day, Mr. Cavendish?" He answered, "We will have a leg of mutton." The housekeeper replied, "But surely a leg of mutton will not be enough." "Very well then," remarked Cavendish, "we will have two legs." Although Cavendish was one of the wealthiest men of his time he lived very frugally and devoted most of his time to performing chemical experiments.

[2] Eighteenth century name for nitrogen.

[3] William Ramsay was born at Glasgow in 1852 and after studying at Glasgow, Heidelberg and Tubingen, he became a lecturer at Glasgow University and later Professor of Chemistry at University College, Bristol. In 1887 he occupied the Chair of Chemistry at University College, London, a position he filled until his retirement in 1912. During the last twenty years of his life honours were pressed upon him by nearly every scientific society of the world. He was created a K.C.B. in 1902 and in 1904 was awarded the Nobel Prize for chemistry. From a "precocious and dreamy youth", as he described himself, Ramsay became the most brilliant chemist this country has possessed. His reputation depends upon his manipulative skill in dealing with minute quantities of gases. An account of his discoveries on radioactivity will be

phosphoric oxide and finally removing the nitrogen by passing through a tube packed with heated magnesium.

At the anniversary meeting of the Chemical Society on March 27th, 1895, a further surprise awaited the chemical world. Ramsay announced the discovery of another new gaseous element, similar in properties to argon, that he had isolated by boiling a rare mineral termed clèveite with weak sulphuric acid. This new gas gave a spectrum similar to that of the metal sodium; closer investigation showed that it was identical with an element that had been detected in the sun's chromosphere by Janssen in 1868, and to which the name *helium* (from the Greek *helios*, the sun) had been given by Sir Norman Lockyer. Subsequent research showed that helium is contained in a large number of minerals, especially those containing the radioactive elements uranium, thorium and radium. In 1895 Kayser announced the discovery of helium in the air.

Argon and helium baffled the chemists because of their chemical inertness. Where could they be put in the Periodic Table? The combining capacity or *valency* of the atoms in Group I is 1, and this property varies from group to group. But argon and helium form no compounds; they have no combining capacity, that is they have zero valency. A new group termed the Zero Group, was accordingly added to the Periodic Table to accommodate the new elements of the atmosphere, helium being placed at the head of the group and argon two places lower. This arrangement left a gap in the Zero

GROUP O or Zero Group	GROUP I
Helium (4)	Lithium (7)
— (20)	Sodium (23)
Argon (40)	Potassium (39)

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found in the next chapter. Very sociable, musical and possessed of the gift of tongues—he could lecture in English, French, German and Italian—Ramsay was beloved by his colleagues and by all those who came in contact with him. Early in 1916 he contracted an incurable disease and died in July of the same year.

Group corresponding to an element of atomic weight 20. A laborious search was made by Ramsay and Travers for the missing element, which might never have been discovered but for Mendeléeff's brilliant generalisation. Minerals and waters from mineral springs were exhaustively examined without yielding any trace of a new element and unsuccessful attempts were also made by Ramsay and his assistants to resolve helium and argon into two or more elements. At this time new methods were introduced for liquefying air, and by the distillation of a large quantity of this substance Ramsay and Travers isolated a gas having about twice the density of argon. This new gas they termed *krypton* (from the Greek *krypton,* hidden). In 1898 a fourth new element was obtained by the distillation of crude liquid argon. This proved to be the missing element of atomic weight 20; it received the name neon (from *neon,* new). The neon proved to be impure, being mixed with helium, and it was separated from this element by cooling down with liquid hydrogen. The neon solidified, whilst the helium, still a gas, was pumped off. Ramsay and Travers finally discovered another gas in the least volatile portions of liquid krypton and this was named xenon (from *xenon,* the Greek for stranger).

These new elements were fitted into a group of their own in the Periodic Scheme.

ZERO GROUP	GROUP 1	GROUP 2
Helium 4	Lithium 7	Beryllium 9
Neon 20	Sodium 23	Magnesium 24
Argon 40	Potassium 39	Calcium 40
Krypton 84	Rubidium 85	Strontium 87
Xenon 130	Caesium 133	Barium 137
Radon 222	—	Radium 226

The story of radon, the last of the rare gases to be discovered, belongs to another chapter. The discovery of a whole series of elements by one investigator is no mean achievement. This is one of the triumphs of British science that has not been surpassed and perhaps not equalled in the history of chemistry.

The rare gases form an interesting group because of their inertness; they refuse to undergo any chemical change, probably because in their atoms the outer ring of electrons contains a stable number such as 8. All occur in the atmosphere from the extent of 1 per cent (argon) to ·0000006 per cent (xenon). Argon has been used for filling the best metal filament electric bulbs, as it enables the tungsten filament to be run at a higher temperature than in a vacuum bulb without causing the bulb to become blackened by volatilised tungsten. Helium, being very light and non-inflammable, is used in filling airships; any possibility of fire or explosion is thus eliminated. When first discovered helium cost something like £300 a cubic foot to produce. Now it is manufactured for less than 2½d. a cubic foot from the natural gas that occurs in some of the American and Canadian oilfields. Liquid helium, which boils at —252·5° C. (252·5° C. below zero), has the lowest boiling point of any known substance and by its rapid evaporation a white solid can be obtained at a temperature of —272° C. In America, where large supplies of helium are available, the gas is supplied to men working in compressed air under water. When brought to the surface too quickly the men often collapse, owing to the nitrogen in the air which has dissolved in their blood under pressure, being suddenly released. This interferes with their lungs and may affect the brain. Helium is much less soluble than nitrogen, and if the locks where the air pressure is reduced are filled with a mixture of helium and oxygen instead of air (i.e. nitrogen and oxygen) this danger in minimised. Divers can also use a mixture of oxygen and helium.

Neon is used for filling electric light tubes employed in advertising signs; they emit an arresting orange-red light. Neon-filled lamps are used as fog-lamps (*Plate* 8), and recently the Lympne aerodrome has been fitted with sixteen neon tubes, each 20 feet long, with a total candle power of 6,000. Neon is also used in sparking-plug testers.

The discovery of a large number of elements would not have been possible without the instrument known as the spectroscope. Indeed, the recognition of the rare gases was only achieved by its use. The gases were enclosed in special tubes under low pressure, an electric discharge passed, and the light emitted analysed with a spectroscope. When white light or sunlight is passed through a prism it is broken up into a series of coloured rays called a spectrum, and the apparatus used for producing and observing spectra is termed a spectroscope. If the light emitted by an incandescent vapour or gas be examined by the spectroscope, a spectrum, consisting only of isolated bands or lines of different colours will be seen, in other words a line spectrum is obtained. Every element has its own characteristic spectral lines and no two lines given by different elements occupy the same position in the spectrum. The spectrum of an element thus serves for its identification. This is the principle underlying spectrum analysis, introduced by Bunsen and Kirchhoff in 1850. By means of the spectroscope the chemist can reveal the presence of minute quantities of an element that would defy detection by ordinary analytical methods. Even $\frac{1}{8000000000}$th of a gram of sodium can be detected spectroscopically. It has been possible to deduce the presence of some thirty-four elements in the sun's atmosphere by an examination of its spectrum.

In 1860 Bunsen and Kirchhoff, whilst examining the mineral waters of Dürkheim, in Germany, evaporated about forty tons of the water, and after removing all the metals present except sodium and potassium, they submitted the residue to spectroscopic analysis. Two splendid blue lines were observed, and as they did not correspond to those given by any of the then known elements, Bunsen and Kirchhoff concluded that they had discovered a new element, which they termed *caesium* (from the Latin *caesius*, sky blue). Shortly afterwards the same investigators discovered a new element in a mineral called lepidolite. The spectrum of a preparation from this mineral gave two reddish-lilac lines, which did not belong to any previously known body. The element corresponding to these lines received the name *rubidium* (from the Latin *rubidus*, darkest red).

It is a curious fact that helium was discovered in the sun before it was known on the earth. In 1868 Janssen described its spectrum; Ramsay discovered terrestrial helium in 1895.

Another element was spectroscopically discovered by Sir William Crookes in 1861 whilst examining some flue dust from a sulphuric acid works. Crookes named it *thallium* (from the Greek *thallos*, a green twig) on account of a characteristic green line in its spectrum. This new element, which in some respects resembles lead, is used to a limited extent in the manufacture of special optical glass. It shows such great diversity of properties that Dumas, the famous French chemist, referred to it as "the ornithorhynchus, or duck-billed platypus, of the metals." Two years after Crookes' researches Reich and Richter subjected a specimen of Freiburg zinc blende to spectroscopic examination and observed a new, bright indigo-blue line. This corresponded to a new element, which received the name *indium*. In 1875 Lecoq de Boisbaudran discovered by means of the spectroscope the rare element *gallium*—Mendeléeff's eka-aluminium—in a zinc ore from the Pyrenees.

The study of X-ray spectra and atomic numbers has led to the discovery of no less than four new elements during the last decade. With our knowledge of atomic numbers we can line up the elements like a company of soldiers, call the roll, and see how many are missing. The total number of elements is 92; there is room for no more in the Periodic Table. Moseley's work enabled the atomic numbers of the elements to be calculated from the frequency of the X-ray spectrum lines and from the atomic numbers we can find out if there are any missing elements. If two known elements with successive atomic weights have atomic numbers differing by unity, there is no possibility of another element coming between them. But if the atomic numbers differ by more than one, another element must come in between the two elements. Thus it was found that *lutecium*, a member of the group known as the rare earths, had an atomic number of 71, and tantalum, the next element in order of atomic weight, had an atomic number of 73. The existence of a missing element with an atomic number 72 was clearly indicated, and this was discovered in zirconium minerals by Coster and Hevesey in 1923. They detected in the X-ray spectra of zirconium preparations lines characteristic of an element of atomic number 72. This received the name *hafnium*, from Hafnia, the old name for Copenhagen. Hafnium has a high melting point and high electronic emissivity; two patents have been applied for its use in lamp filaments and radio-tubes.

Five elements were still missing in 1923. Three of these have since been discovered by X-ray spectroscopy. In 1925 Noddack discovered two new elements in minerals containing platinum and tantalum. They were named *rhenium* and *masurium.* In 1926 Hopkins in America identified the X-ray spectrum of a new element belonging to the rare earth group of elements. This new element, called *illinium*, is present in the mineral monazite, the raw material from which gas mantles are made. It was named *florentium* by certain Italian chemists who claimed to have discovered it in 1924. Two elements are still missing with atomic numbers 85 and 87 respectively.[1]

Moseley's atomic numbers suggest that the chemical elements belong to one family and that each element is in some way related to the others. The wheel of thought has turned full circle. The Greek idea that there is one primordial element, or *proto hyle*, from which all matter has sprung is no longer a phantasy of the philosophic mind. In 1816 Prout attempted to show that the atomic weights of the elements were exact multiples of the atomic weight of hydrogen, (i.e. unity) and concluded that: "we may almost consider the *proto hyle* of the ancients to be realised in hydrogen". Prout's hypothesis, that the elements are aggregates of the atoms of primordial hydrogen, could not be substantiated experimentally when it was apparently found that most of the atomic weights were not even approximately multiples of that of hydrogen. Recent investigation has shown that elements with fractional atomic weights are really mixtures of simple bodies with whole number atomic weights; such elements we call isotopes. Taking isotopy into consideration, the atomic weights of most of the commoner elements do approximate very closely to whole numbers, and W. D. Harkins of America has suggested that elementary atoms are built up from a common unit of atomic weight approximately 1, that is from hydrogen. If oxygen is composed of sixteen hydrogen atoms, the atomic weight of oxygen should be sixteen times that of hydrogen, whereas the actual relative atomic weights are 15·875 : 1. This means that the atomic weight of oxygen falls short of an exact multiple of one by $\frac{16-15{\cdot}875}{16} \times 100$, or $-0{\cdot}77$ per cent. Harkins explains this on the assumption that a *packing effect* occurs in the nucleus of the atom, the protons and electrons being packed so closely that the energy changes produced affect the mass of the protons. The packing effect for the majority of the more abundant elements is of the same order, i.e. −0·77 per cent. Such a constant deviation suggests that the hydrogen atom is one of the fundamental units in the atomic architecture of the different atoms. Aston has shown that the mass of the hydrogen nucleus or proton is nearly 1 when packed into the nucleus of other atoms, although it is 1·008 when free.

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[1] See, however, p. 62 (note)

Harkins considers that the helium nucleus is an aggregate of four closely packed hydrogen nuclei and two electrons. If the mass of the hydrogen atom is 1·008 that of the helium atom should be 1·008 × 4=4·032, whereas it is 4. The loss in mass of ·032 is due to the packing effect (−0·77 per cent). When four hydrogen atoms form a helium atom, the excess of mass appears as energy. It has been calculated that the amount of energy liberated by the transformation of 1 cubic foot of hydrogen into helium would convert nearly a million pounds of ice into steam. The change of hydrogen into helium may account, in part, for the great heat of the sun in which both elements are present. Harkins further supposes that the elements of even atomic weight are composed of helium nuclei—secondary units in atomic architecture—and that those of odd atomic weight are composed of helium nuclei and something of mass three, probably a kind of condensed or polymerised hydrogen (H_3). Elements of even atomic weight follow the plan nHe, where n is a whole number and He the helium nucleus; those of odd atomic weight are composed of nHe + H_3. Bearing in mind that the mass of the helium atom is 4 (He=4) and that of the hydrogen atom is 1 (H=1), the first two series of the Periodic Table may be written:

He 4 He=4H	Li 6·94 He+H_3	Be 9·02 2He+H	B 10·8 2He+H_3	C 12 3He	N 14 3He+2H	O 16 4He	F 19 4He+H_3
Ne 20·2 5He	Na 23 5He+H_3	Mg 24·32 6He	Al 26·97 6He+H_3	Si 28·06 7He	P 31·03 7He+H_3	S 32·06 8He	Cl 35·46 8He+H_3

Harkins' suggestions have received support from the work of Aston and Rutherford. Aston's positive ray analysis has shown that all atomic weights, with the exception of that of hydrogen, are whole numbers. Fractional values previously accepted (e.g. chlorine, 35·5) were averages due to the presence of isotopes. The existence of the hydrogen isotope H_3, first detected by Sir J. J. Thomson, has been confirmed by Aston, and its atomic weight ascertained (3·026). Rutherford found that hydrogen was released from elements of odd atomic weight when they were bombarded with X-rays.

What is the origin of hydrogen and helium? This is purely conjectural. It is supposed that long before the earth existed a kind of extremely hot ultragaseous *protyle*, or primal form of matter, filled space, and that this gradually cooled and condensed into the lightest known elements. Hydrogen and helium formed first, and from these were born the other elements. The last elements in the scale of creation were the radioactive ones—uranium, thorium and radium. This explanation is extremely likely in view of the fact that if the different suns and stars that have been examined be arranged in a series, the order of the appearance of the elements in the cooling stars is approximately the order of their increasing complexity as deduced from the magnitude of their atomic weights. The lightest elements such as hydrogen and helium only appear in the hotter stars; in the cooler stars the metals magnesium, calcium and iron make their appearance. Astronomers have shown that as nebulae grow older and cooler, more spectral lines can be observed indicating the appearance of new elements.

CHAPTER IV

THE STORY OF RADIUM

In 1896, a year after Röntgen's discovery of the X-rays, Henri Becquerel of Paris discovered the property known as radioactivity. During the course of researches on the phosphorescent properties of certain minerals he found that uranium preparations affect a photographic plate wrapped in black paper, and he inferred that uranium must emit rays capable of passing through opaque paper to ordinary light. Becquerel subsequently discovered that uranium compounds give off rays that produce fluorescence in certain bodies (e.g. zinc sulphide), penetrate thin sheets of metal, and discharge an electroscope. This new radiation, termed the Becquerel rays, proved to be similar in many respects to the X-rays. Both render gases through which they pass conductors of electricity, that is, they ionise gases. The degree of ionisation can be measured quantitatively by a gold leaf electroscope, which consists of two slips of gold leaf gummed to a piece of metal suspended vertically. Normally the gold strips hang parallel, but if they are charged with electricity they mutually repel one another and fly apart. Under ordinary conditions the gold leaves of the electroscope will remain apart in air because this is a bad conductor. But if a substance emitting Becquerel rays be brought near the leaves, they collapse owing to the charge leaking away through the air which has been ionised by the rays. The time taken for the electroscope to collapse is a measure of the ionising power of the substance.

Two years after Becquerel's researches Schmidt and Madame Curie discovered that thorium compounds produce effects similar to those shown by uranium compounds. Both uranium and thorium were said to be radioactive. A well known French writer once said: "France has two geniuses—Rodin and

Madame Curie". This remarkable woman stands out as one of the pioneer workers in radioactivity. She was born in 1867 at Warsaw where her father Dr. Sklodowski taught science. As a young girl she went to Paris to complete her education, not, however, without a hard financial struggle. Her resources were so meagre that she occupied a small back room four stories up a cheap lodging house and contented herself with a diet that consisted largely of bread and milk. Ten cents represented her daily expenses, and this was earned by private tutoring and washing bottles at the Sorbonne, where she eventually became a pupil of Professor Curie. A strong friendship that sprang up between the two led to their marriage in 1895.

After Becquerel's discovery of radioactivity Madame Curie and her husband examined a large number of uranium minerals by means of the electroscope. They found that the electrical conductivity or ionisation of the air induced by the rays from a uranium compound depends upon the amount of uranium present. All uranium compounds, whatever their source, ionise the air, and the degree of ionisation, which can be found by means of the electroscope, is a measure of their radioactivity. Madame Curie observed that uranium itself is more radioactive than any of its compounds except pitchblende or uraninite (U_3O_8), native chalcolite (copper uranyl phosphate), and carnotite, which are from two to four times as radioactive as the same amount of uranium that they contain. Yet when Madame Curie prepared chalcolite artificially in the laboratory it proved to be far less radioactive than the naturally occurring mineral. She concluded that the strong radioactivity of the pitchblende and other uranium minerals is due to the presence of minute quantities of an exceptionally radioactive substance, and in 1898 she laboriously separated the known constituents of Bohemian pitchblende with the view of isolating this active substance.

Pitchblende is a dark mineral consisting chiefly of uranium oxide and smaller amounts of lead—a very significant fact, as we shall see later—bismuth, calcium, barium, copper, iron and other metals in the combined state. The main source of pitchblende was originally the Joachimstal mine in Bohemia; important deposits of the mineral carnotite occur in Colorado and Utah, U.S.A. A large quantity of pitchblende from the

Joachimstal mine was separated from earthy impurities and presented by the Austrian Government to Madame Curie and her husband. Starting with something like a ton of pitchblende residues they separated the bismuth and the barium from the other metals. The bismuth, which was separated as bismuth sulphide, appeared to contain a highly radioactive body and this was obtained free from bismuth by heating *in vacuo* to 700° C. By further treatment a substance 400 times as active as uranium was obtained, and this was named *polonium* in honour of Madame Curie's native country. Another active substance was associated with the barium obtained from the pitchblende. Barium can easily be separated from solution by the addition of sulphuric acid which throws down a white insoluble precipitate of barium sulphate. The active substance accompanied this and by converting the sulphate into the chloride it was found that the barium chloride had a higher solubility in water than the chloride of the active substance. Repeated crystallisation of the mixture enabled Madame Curie to separate a highly radioactive body; this was called *radium*. Giesel discovered that its separation from barium could be accomplished more easily by the repeated crystallisation of the bromides of the two elements. From a ton of pitchblende a quarter of a grain of radium was finally obtained. About one part of radium is present in 5,000,000 parts of pitchblende, that is 300 tons of pitchblende would be required to obtain an ounce of radium.

Radium is several million times more radioactive than uranium. Its spectrum, atomic weight and general chemical properties show it to be a member of the alkaline earth metals, which includes barium and calcium. In view of its scarcity and difficulty of isolation radium must of necessity be a scientific curiosity and a highly costly one at that. At the time of its discovery a grain ($\frac{1}{480}$ of an ounce) of radium cost some thousands of pounds. Until 1924 it cost £2,000 a grain or £960,000 an ounce. In that year the cost dropped to nearly half this owing to new sources of the metal being discovered. The principal sources of radium are pitchblende and carnotite. Carnotite is also worked as a source of vanadium, a metal used for increasing the elasticity and tensile strength of steel. Valuable deposits of radium minerals have recently been discovered in the Belgian

Congo. Besides occurring in pitchblende, minute traces of radium have been found in many minerals and rocks by means of delicate electroscopes. Joly has estimated on the basis of his analysis of sea water that in the ocean bed there are well over a million tons of it. All uranium ores contain traces of radium, which is supposed to have been formed by the breaking down or disintegration of uranium atoms. Metallic radium was not isolated until 1910 when Madame Curie prepared it by the electrolysis (i.e. decomposition by electricity) of radium bromide with a mercury cathode. The alloy of mercury and radium so obtained was then heated under reduced pressure in an atmosphere of hydrogen to remove the mercury and radium remained.

Radium itself is a bright shining metal that gradually tarnishes in air and like the metals sodium and calcium it decomposes water with the formation of hydrogen. The compounds of radium, the chloride and bromide for example, gradually decompose water when dissolved in it. This is due to the liberation of energy stored up within the radium atoms; this energy can effect the decomposition of water in much the same way as electricity can. Radium compounds are white when freshly prepared, but on keeping they gradually turn pink.

Radium spontaneously evolves energy in the form of heat and light. It is visible in the dark and induces phosphorescence in certain substances, such as diamonds, zinc sulphide and barium platinocyanide. With the aid of delicate thermometers it is possible to show that radium is a few degrees hotter than surrounding bodies. Curie and Laborde calculated that one gram of radium emits 100 calories[1] per hour; Rutherford obtained the value 130 calories. This means that in one year enough heat is given out by an ounce of radium to boil over seven gallons of water. This liberation of heat and energy goes on almost indefinitely, although there is a limit as we shall see. In the course of its life a gram of radium gives out energy equivalent to $5{\cdot}5 \times 10^8$, i.e. 550,000,000, calories. Since this amount of energy is also produced by burning a ton of coal, radium supplies about a quarter of a million times as much energy as an equal weight of this substance. Matter, which we have formerly considered as inert and only capable of giving back energy supplied to it, is a huge reservoir of latent energy. This infra-atomic energy can be expended without borrowing anything from without. The constant emission of energy is one of the riddles of radioactivity. It appears to contradict the two fundamental dogmas of science, the conservation of mass and the conservation of energy, and it favours the existence of a perpetual motion machine. The principle of the conservation of energy implies that energy cannot be created or destroyed; we can transform energy from one kind into another, e.g. chemical into electrical energy and this in turn into heat energy, but we cannot get more energy out of a system than we put into it. In other words we cannot create energy. Yet we have the spectacle of radium continually pouring out energy without undergoing any apparent change. It comes from the radium atoms. When their heavy nuclei break up the energy stored within them is set free and causes the remarkable phenomena associated with radioactive substances. Possibly other elements are doing this, but at a much slower rate.

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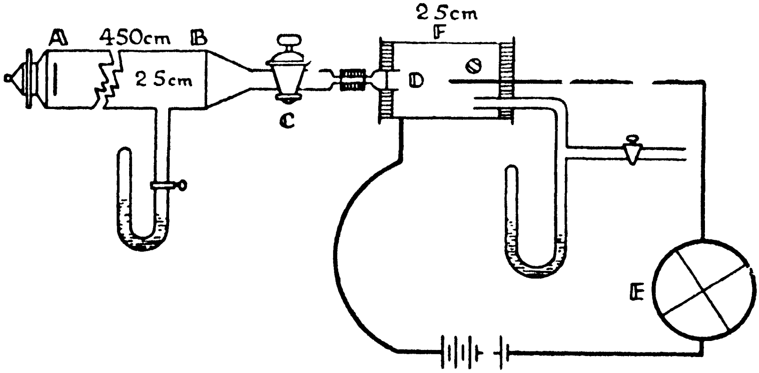
[1] A calorie is the quantity of heat required to raise the temperature of 1 gram of water from 0°C. to 1°C.

All uranium and radium compounds spontaneously emit three types of rays—the *alpha* (α)-, *beta* (β)-, and *gamma* (γ)- rays. They are responsible for the radioactive phenomena. They fog a photographic plate, ionise gases and cause fluorescence in certain materials. The first analysis of these complex radiations was made by Rutherford. Under the influence of a magnetic field the rays can be sorted out; the α-rays are slightly deflected; the β-rays suffer considerable deflection; while the γ-rays suffer no deflection at all. The rays also differ in their penetrative powers. A layer of aluminium 0·01 cm. thick will filter out the α-rays, but the β- and γ-rays pass on. A layer of aluminium ·5 cm. thick stops both α- and β-rays; the γ-rays pass through it. The α- and β-rays are really charged particles projected at a high velocity from the nucleus of the radioactive body. The γ-rays are a form of wave motion or undulation of the ether, produced by the impact of the β-rays on matter, in the same way as X-rays are formed when the cathode rays bombard an anti-cathode.

The α-particle, which carries two positive charges, was shown by Rutherford to be a charged helium atom expelled from radioactive elements with a velocity of about one-tenth that of light, i.e. about 18,600 miles per second. Originally uncharged, the α-particle develops its charge as it passes through matter. It corresponds to the positive rays produced in a vacuum tube by an electric discharge. The α-rays possess such enormous energy that their collisions with matter can be made visible under suitable circumstances. If the rays from a speck of radium are allowed to strike a screen coated with zinc blende (zinc sulphide) bright flashes of light are produced and these can be made visible from above by a lens. This is the principle of Sir William Crookes' *spinthariscope* (Fig. 1). When the α-particles strike the screen their energy is liberated and this manifests itself in the form of heat and light. Each impact due to an α-particle is accompanied by a flash of light. The effect produced is something like a group of shooting stars or a swarm of fireflies on a dark night. Rutherford and Bragg have shown that the ionisation produced by radium and radioactive bodies is the consequence of an α-particle within the atom and depends for its amount on the time taken for the α-particle to cross the atom. It has been found that the stopping power of an element for the α-particle varies with its atomic number and therefore with the number of planetary electrons.

Rutherford and Geiger have devised an excellent method for counting the α-particles shot off from radium. A radium preparation is fixed in a long evacuated cylinder A B (Fig. 15),



Rutherford & Geiger's Apparatus for counting α - particles

[From Partington's Everyday Chemistry.

FIG. 15

termed the "firing chamber", and the α-particles ejected by the radium shot along the cylinder through a mica window, D, into a brass chamber termed the target or detecting chamber, F. This is connected by a wire, O, to an electrical instrument called an electrometer, E, the pointer of which gives a jump every time an α-particle passes into the detecting chamber. Conditions are so arranged that from two to five particles per minute pass. The needle movements are recorded on a chart (Fig. 16), each jump representing the arrival of an α-particle in the detecting chamber. By simple arithmetic we can calculate the number of α-particles given off per second from one gram of radium. This is in the region of 34,000,000,000.

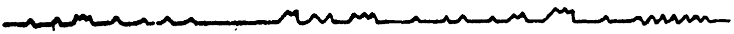


FIG. 16

The β-rays are of the same nature as the cathode rays; they are electrons or negatively charged particles travelling at velocities carying from 60,000 to 178,000 miles per second. The rays have little ionising power, but their penetrating power is very great on account of their high velocity and small mass ($\frac{1}{1834}$ that of a hydrogen atom, which weighs 14×10^{-25} grams). They will readily pass through thick sheets of paper, although half an inch of aluminium is capable of arresting them.

The γ-rays, which are very similar to the X-rays, consist of high frequency vibrations in the ether, and have a wavelength less than 10^{-10}cm. This is less than $\frac{1}{100}$th the wavelength of X-rays. Their exceptionally high penetrating power enables them to pass through 10 inches or more of lead. Far more penetrating are the so-called cosmic rays from outer space with wavelengths 10,000,000 times shorter than those of ordinary light. The origin of these cosmic rays is doubtful. It is probable that they are the result of the building up of atoms in the outermost regions of space; they may be, as Millikan puts it, the birth-shrieks of atoms. The γ-rays of radium are responsible for the fogging of a photographic plate and in part for the ionising effects produced by radium. They ionise gases by knocking the electrons out of the atoms.

The chemical effects produced by radium are interesting and unexpected. By means of the energy locked up within its atoms it can convert oxygen into ozone, decompose water, reduce the silver bromide emulsions on photographic plates, and colour common glass. Madame Curie noticed that glass gradually becomes coloured violet when left in contact with radium. It will char paper, harden vaseline and render rubber quite brittle. The physiological action of radium is even more striking. One of the earlier workers on radioactivity who carried an unprotected radium preparation in his waistcoat pocket sustained severe burns that developed into painful sores. A new line of research—radio-therapy—was thus born. Although radium preparations can be handled without any immediate harmful effects, sores may develop on the skin of those who constantly handle the substance. For this reason it is stored in lead boxes and suitable screens are used to prevent the rays from reaching the skin of the experimenter. Radium is used in the treatment of cancer where the disease is not deep-seated and is amenable to treatment. The results, however, are not so satisfactory as was originally anticipated and the testimony of medical experts is not unanimous. The gas or emanation that is constantly being produced by radium is often used for therapeutic purposes. It is pumped off into small glass tubes which are inserted into the diseased tissue. It is stated that rodent cancer in its early stages can be cured by radium treatment, and scars, tumours and certain complaints of the eye have also been treated successfully. Radium rays sterilise seeds and spermatozoa and they are fatal to micro-organisms. The therapeutic uses of radium have been extensively investigated at the Radium Institute of Paris, and at the Crocker Research Institute of New York.

Some of the earlier workers on radioactivity noted that substances in the neighbourhood of radium preparations became themselves radioactive, and Rutherford suggested that the effects were due to the emission of a radioactive gas or emanation from the radium. In 1900 this gas was isolated and shown to be a missing member of the family of rare gases to which helium and argon belong. Ramsay subsequently called it *niton* (Latin *nitens*, shining) because it can be condensed to a phosphorescent solid. More recently it has been termed *radon*. Thorium and uranium also give off similar radioactive gases.

Radon has all the properties of an element and like the rest of the rare gases refuses to enter into chemical combination with any known substance. Consequently it has no chemical properties. Owing to the extremely small quantities available, great manipulative skill is required in experiments with it. One gram of radium furnishes 3 cubic millimetres of radon in about a week. Very few experimenters have more than half a grain for experimental purposes and this would only yield ·1 of a cubic millimetre of the gas. It is constantly radiating energy, three times as much energy in fact as the radium from which it is derived. A pint of radon—and to obtain this amount half a ton of radium would be required—radiates as much energy as a hundred arc lamps for several days. As Rutherford has pointed out, no vessel could hold such a quantity of the substance, which would melt and vaporise everything known. In spite of the small amounts available, Ramsay determined the density of radon using a balance capable of weighing $\frac{1}{500000000}$ of a gram. He only possessed a tenth of a cubic millimetre of the gas, and this occupied a volume smaller than a pin's head. Its density proved to be greater than that of mercury vapour.

Radon has a short life and a merry one. If we keep it sealed up in a tube for several days we find that its activity gradually decreases; in nearly four days (92 hours) it will only possess half its initial activity. After it has been extracted from radium, either by heating or bubbling air through a solution of a radium compound, the radium loses some of its activity. Actually the so-called activity of radium is largely due to the radon it is continually producing. But the radon, once separated from the radium, gradually *loses* its activity, whilst the radium gradually *regains* its activity. This may strike the reader as a strange paradox. Let us suppose that several weeks have elapsed after the extraction of some radon from a compound of radium and that the latter, which has now regained its activity, is dissolved in water and a current of air rapidly blown through. A fresh quantity of radon would be produced. This process can be repeated almost indefinitely. While the radon decays and loses its activity, more is being spontaneously produced by the radium. No known process is capable of accelerating or retarding the rate of these radioactive changes; they occur at the same rate at the temperature of molten iron as they do at temperatures in the region of 200° below zero. Radioactive changes are thus different from ordinary chemical reactions. In 1902, Ramsay and Soddy observed that radon spontaneously decomposes into a radioactive solid and the gas helium. The radon loses its characteristic spectrum and that of helium appears in its place. It was also discovered that the α-particles which are discharged when radium gives rise to radon are charged helium atoms. Radon similarly emits α-particles, which become ordinary helium atoms on losing their positive charge.

From whence comes the energy associated with radium and radioactive bodies? One possible explanation is that they are energy transformers, taking up energy from outside, and changing it into another form, which is then liberated again. They would then be like a steam-engine converting heat into mechanical energy. Such a view does not fit in with the facts; there is no evidence that radioactive bodies transform outside energy. Radioactivity is an atomic property, and it results from the instability of certain atomic systems. The atoms of all radioactive elements are heavy and possess a complicated structure—radium for instance has 226 protons and 138 electrons. Such a complex structure, although linked by forces of tremendous power, is very unstable, and both protons and electrons are liable to be ejected at great speeds; in other words, the atom explodes or disintegrates spontaneously with intense violence. The energy liberated comes from within the atom and results from the protons and electrons striking matter when they are travelling at enormously high velocities. But the explosion does not take place all at once, as it does in the case of an explosive such as T.N.T. or nitroglycerin. A fraction only explodes in a small interval of time and leaves behind a new kind of radioactive atom. Radioactivity is, in effect, a manifestation of a series of atomic explosions. Some radioactive elements shoot out a high-speed negatively charged particle with almost neglible mass; this is the unit negative charge of electricity or electron, generally called a β-particle. Others shoot out a particle with a mass four times that of the hydrogen atom, bearing two positive charges of electricity, and with a velocity about one-tenth that of light; this is the α-particle or charged helium atom, and in virtue of its mass it possesses greater energy than the β-particle. The α- and β-particles are fragments of the atomic explosion, and the remaining part of the atom is consequently a new chemical individual or a new type of chemical element. In a gram of radium bromide are a hundred million billion (10^{20}) separate radium atoms and one two-thousandth of these disintegrate yearly; so that in every second about two thousand million radium atoms disintegrate and eject some small multiple of this number of α- and β-particles. Man cannot hasten this spontaneous decomposition; he can only observe it. If he could hasten the process he would have a source of power so potent that a few pounds of a radioactive element could be made to light a city for a year or drive the machinery of factories and ships.

In radioactive changes one type of atom is spontaneously transformed into another with the liberation of a relatively large quantity of energy. The radioactive elements fall into three families. The atoms of the parent element of each family emit α-particles and become atoms of a different element; both can be separated by analytical methods. The atoms produced are radioactive and they in turn disintegrate into atoms of a third element. These, if radioactive, will be transformed into atoms of a fourth, and so on until an element is reached that is not radioactive, that is, an element whose atoms are stable. As a result of its disintegration a radioactive body will beget several other radioactive bodies which bear the same relation to it as a father does to his son, grandson, great-grandson and so on. At any particular moment there exist together the unchanged radio-element, its products of disintegration and the products of disintegration of these. Although the rate of disintegration for any particular radioactive element is found to be constant, it varies from element to element. Thus Actinium-A is transformed into Actinium-B in the incredibly short period of two-thousandths' of a second; yet uranium takes trillions of years for its complete disintegration.

Radioactive elements do not violate the law of conservation of energy. The energy that they radiate is the difference between the internal energies of the original and the resulting atoms. Although the energy emitted by the breaking down of heavy nuclei is continuous, it must gradually decrease in intensity, because for every atom disintegrating there is one atom less in the original body. If only the chemist could hasten the rate of radioactive changes he would add another weapon to his armoury—namely atomic energy. The atoms of radioactive bodies have tremendous stores of potential energy, far greater than that developed during ordinary chemical reactions. In the words of Soddy:

> Could the energy steadily diffused in the transformation of radioactive elements be harnessed by man, and the rate of progress being made justifies the belief that some day this will be done, we will see a transformation of the standard of life incomparably beyond that brought by the harnessing of steam. . . . Control by man of the atomic energy thrown off by radioactive elements—in a manner similar to the way that ordinary chemical processes such as the combustion of coal are now controlled—is the step which science has yet to take.

If we could only harness the atomic energy of a pound of uranium it would propel a liner across the Atlantic, but under ordinary conditions uranium would take billions of years to liberate this energy. It is quite possible that if we could use atomic energy it might manifest itself in a totally uncontrollable form, possibly in the form of an explosive reaction or as a powerful radiation baffling the wits of man to arrest and handle. It is thought possible that the so-called cosmic rays have their origin in the combination of lighter atoms to form heavier ones in space. If only it were possible to make four hydrogen nuclei, i.e. four protons and two electrons, combine to form helium, then the formation of an ounce of helium produced in this way would be accompanied by enough energy to run a 100 horsepower engine for eight years. But we are far from being able to build up or break down elements at will. In certain cases it has been possible to knock electrons out of atoms of different elements by means of swiftly flying α-particles but the process is not a general one.

Sir Oliver Lodge has compared the breaking up of the complex atoms of radioactive bodies to the contraction of a nebula:

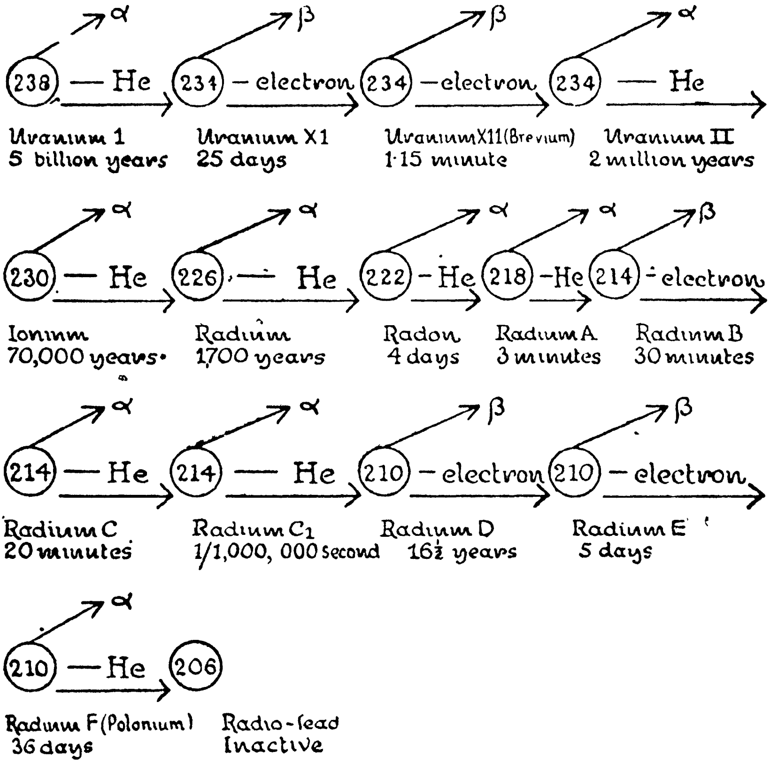
Roughly, the process may be likened in some respects to the condensation or contraction of a nebula. The particles constituting the whirling nebula fall together until the centrifugal force of the peripheral portions exceeds the gravitative pull of the central mass, and then they are shrunk off and left behind, afterwards agglomerating into a planet, while the residue goes on shrinking and evolving fresh bodies and generating heat. A nebula is not hot, but has an immense store of potential energy, some of which it can turn into heat, and so form a hot central nucleus or sun. A radium atom is not hot, but it has an immense store of potential energy in proportion to its mass, for it is controlled by electrical, and not gravitational forces.

After radium breaks down into radium emanation or radon, this in turn suffers disintegration. The nucleus of its atom breaks up and gives rise to that of a further radioactive element, liberating energy in the process. This new element, termed radium A, also suffers breakdown, and we finally get a complex series of elements, all derived from the parent element radium. The final product of disintegration will not be radioactive. It also follows that the elements formed by the spontaneous disintegration of unstable elements will have lower atomic weights than their progenitors. Radon disintegrates into helium and a solid which is deposited on surfaces exposed to the gas. This solid is known as the *active deposit* and it gives rise to successive transformation products as well as to α-, β-, and γ-rays. There are at least nine successive products in passing from radium to its final product of disintegration, which is an isotope of lead. Besides being the parent of a long line of elements, radium is also a great-great-great-grandchild, and traces its lineage back to uranium, the parent of some twenty-four elements. A genetic relationship between uranium and radium was suspected when these two elements were always found closely associated together in nature and invariably in the same proportions (3,400,000 : 1). After a very patient piece of research Boltwood and Soddy proved that radium is continually being produced by uranium, although the change is not a direct one; elements termed respectively uranium I, uranium X, uranium X_2 (brevium), uranium II and ionium come first in the line of succession. Radium is the great-great-great-grandchild of uranium and the direct offspring of the element ionium. It is also interesting to note that the existence of polonium, one of the disintegration products of radium, was one of the undiscovered elements predicted by Mendeléeff, and so small are the quantities of it that have been isolated that Mendeléeff's predictions still represent all that we know about some of its properties.

If an α-particle—which we know is a helium atom of mass 4 carrying a double positive charge—is expelled from an atom of a radioactive element, the mass of the resulting atom will be 4 less than that of the parent; its atomic number will also be diminished by 2. Consequently the new element will occupy a space in the Periodic Table *two places lower* than its parent. Similarly, when a radioactive element expels a β-particle, a negatively charged electron is shot out from the nucleus and as a negative charge lost is clearly a positive charge gained $(- -1 = +1)$, the excess of protons over electrons in the nucleus is now increased by 1. In other words, the new element occupies a position in the Periodic Table *one place higher* than its parent. Radium emanation or radon is formed from radium by the loss of an α-particle; radium is in Group II, radon in the Zero Group. The expulsion of a β-particle from radium E, an elementin Group V, gives rise to radium F (polonium) in Group VI.

The accompanying table (Fig. 17) represents the transformations that occur in passing from uranium to radio-lead. The numbers within each circle give the atomic weight of the element; each α-ray represents the loss of a helium atom and each β-ray the loss of an electron.

Beneath each element is given a time, varying from a millionth of a second to billions of years. These times give some idea of the rate at which one element disintegrates into another. From experimental data the *period of average life* of a radioactive element can be calculated. This is the time taken for complete disintegration assuming that the element decomposes at a constant rate equal to its initial rate of decay. It should be realised that the atoms disintegrating first have a far shorter period of life and those disintegrating last have a longer total period than the average. Only a certain fraction of the atoms of a certain radioactive element decay in a given time and consequently as the number of the original atoms which are left diminishes, the number of atoms decaying in the given time gets less and less. For complete decay an infinite time would be required. Cameron illustrates the meaning of average life period as applied to radioactive bodies in the following way: If a church at a fixed time contains a number of people of different ages, then, given the number of years each person will live after leaving the church, the average life of the congregation is reckoned from the time fixed by that church attendance. The average life period of radium is 2,500 years; in other words, in one year only $\frac{1}{2500}$ of the original would have decayed. It is more convenient to find the *half-life period* of a radioactive element or the time required for the disintegration of half of the original amount. These are the figures given in the above table. The half life period of radium is 1,700 years. This means that a given sample of

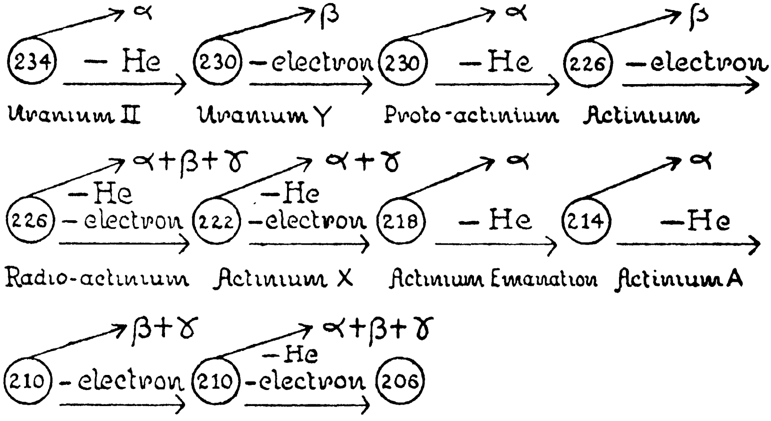

α
β
β
α
238 — He
234 — electron
234 — electron
234 — He
Uranium 1
5 billion years
Uranium X1
25 days
UraniumX11(Brevium)
1·15 minute
Uranium II
2 million years
α
α
α
α
β
230 — He
226 — He
222 - He
218 -He
214 - electron
Ionium
70,000 years
Radium
1700 years
Radon
4 days
Radium A
3 minutes
Radium B
30 minutes
α
α
β
β
214 — He
214 — He
210 - electron
210 - electron
Radium C
20 minutes
Radium C1
1/1,000,000 second
Radium D
16½ years
Radium E
5 days
α
210 — He
206
Radium F (Polonium)
36 days
Radio-lead
Inactive

THE URANIUM-RADIUM SERIES

FIG. 17

radium will only be half changed in 1,700 years and that 1,700 years later still half of what remains will have decayed. Radium C has a half life period of only $\frac{1}{1000000}$ of a second; the half period of uranium is five billion years.

Uranium, besides being the progenitor of radium, also gives rise to another radioactive element called actinium. This was discovered in 1899 by the French chemist Debierne, whilst working up uranium residues for Madame Curie's researches, and Rutherford later showed that it is a descendant of an element named uranium II, the great-grandchild of uranium. About 8 per cent of the atoms of uranium II disintegrate into uranium Y and by loss of electrons this becomes proto-actinium, the parent element of actinium. Actinium finally breaks down forming a series of products, the last of which is an isotope of lead.

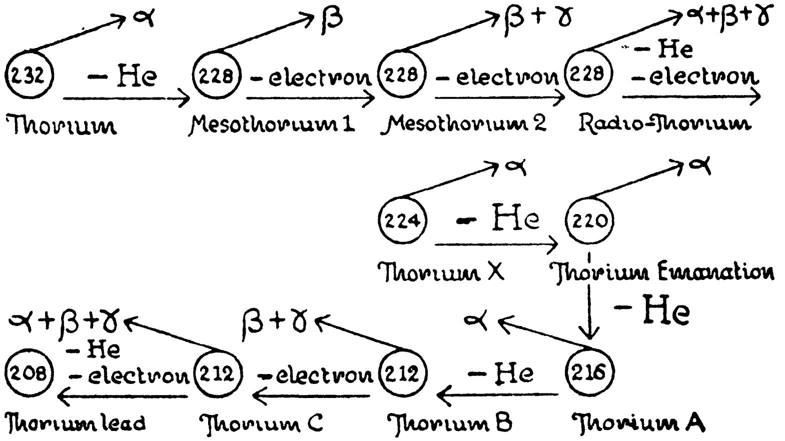

α
234
— He
Uranium II
β
230
—electron
Uranium Y
α
230
—He
Proto-actinium
β
226
—electron
Actinium
α+β+γ
—He
226
—electron
Radio-actinium
α+γ
—He
222
—electron
Actinium X
α
218
—He
Actinium Emanation
α
214
—He
Actinium A
β+γ
210
—electron
Actinium B
α+β+γ
—He
210
—electron
Actinium C
206
Actinium lead

The ACTINIUM SERIES

FIG. 18

Thorium also gives rise to a number of radioactive descendants, one of them, mesothorium, being an isotope of radium. It is used in place of the latter for making watch dials luminous. Thorium is employed in making gas mantles.

Interesting speculations have arisen concerning radioactivity and the age of the earth. Radioactivity tells us that for billions of years the earth has existed in much the same physical condition as we know it to-day. The known radioactive minerals could not disintegrate and radiate energy for more than eight billions of years. On the other hand a study of radioactivity has shown that some of the radioactive changes occurring in minerals must have taken at least two billion years to come about. By examining the amounts of uranium, helium and lead in certain minerals, their age can be computed from the fact that 1 ton of uranium in a million years gives 7,000 cubic inches of helium and four and three quarter ounces of lead. Specimens of the mineral fergusonite have been shown to be at least 415,000,000 years old by this method. It has also been suggested that the energy emitted by radioactive elements plays an important part in maintaining the heat of the earth, counteracting the effect of radiation by which the earth is tending to cool down. Rutherford has shown that one part of radium in 460 billion parts of the earth would produce as much heat as that lost by radiation. Yet the amount found in rocks is about twenty times this—which means that the temperature of the earth may be actually rising.


α
232
− He
Thorium
β
228
− electron
Mesothorium 1
β + γ
228
− electron
Mesothorium 2
α+β+γ
− He
228
− electron
Radio-Thorium
α
224
− He
Thorium X
α
220
Thorium Emanation
− He
α
216
Thorium A
− He
212
Thorium B
β + γ
− electron
212
Thorium C
α + β + γ
− He
− electron
208
Thorium lead

The THORIUM SERIES

FIG. 19

The radioactive elements appear to be undergoing a kind of spontaneous transmutation that man cannot as yet control. But the alchemists' dream of transmutation—the conversion of one type of matter into another at will—is no nearer realisation to-day than it was in the Middle Ages. There is no conclusive evidence of the conversion of one element into another predetermined by the will of the experimenter. All the radioactive changes go on spontaneously; man cannot start or stop them, nor can he accelerate or retard the processes. Many cases of alleged transmutation have been reported during the present century, although nearly all of them lack confirmation and can be explained by the introduction of impurities derived from the chemicals and apparatus employed.

Since the atoms of different elements appear to be made up from the same fundamental units, there is no inherent objection to the idea of transmuting elements by the addition or removal of these units from atoms. The ninety-two different elements of the world are determined by the difference between the number of positive and negative charges packed into the nucleus. In the words of R. A. Millikan:

> All these elements (are) transmutable ideally at least, into one another by a simple change in this difference. Has Nature a way of making these transmutations in her laboratories? She is doing it under our eyes in the radioactive process—a process which we have very recently found is not at all confined to the so-called radioactive elements but is possessed in very much more minute degree by many, if not all, of the elements. Does the process go on in both directions, heavier atoms being continually formed as well as continually disintegrating into lighter ones? Not on the earth, so far as we can see. Perhaps in God's laboratories, the stars. Some day we shall be finding out. Can we on earth artificially control the process? To a very slight degree we know already how to disintegrate artificially, but not as yet how to build up.

In 1907 Ramsay and Cameron reported that under the influence of radon, copper could be converted into another element, lithium, which they detected spectroscopically. Other workers have failed to confirm this, and attribute the presence of the lithium to impurities in the vessels used. Ramsay further stated that neon could be produced from radon, although Rutherford denies this. He suggests that the neon came from air that leaked into the apparatus. According to Ramsay's theory the α- and β-particles from radium are hurled out at such tremendous velocities that they shatter any stable atoms in their path and convert them into lighter ones.

Ramsay has also described an experiment in which carbon dioxide was produced by the action of radon on thorium compounds. Other investigators, however, are inclined to think that the carbon dioxide came from the grease used in lubricating the stop-cocks of the apparatus.

The transformation of hydrogen into neon under the action of the cathode rays of a vacuum tube is an accomplished fact if we are to believe in the work of Ramsay and his colleagues, Collie and Patterson. The latter subjected calcium fluoride to the action of cathode rays and although calcium fluoride is composed of the elements calcium and fluorine only, these investigators found not only neon, but traces of oxygen and hydrogen in the cathode tubes. New elements made their appearance. Were they a product of modern transmutation, being derived from the heavier atoms of calcium and fluorine under the terrific bombardment of the cathode rays? Or did they diffuse into the apparatus from the air? Further experiments by Strutt and Merton in 1915 failed to confirm Collie's work.

Recent attempts have been made to transmute mercury into gold. In 1924 a German chemist named Miethe announced that mercury can be changed into gold by passing a current of high voltage through a mercury-quartz vapour lamp and a similar claim was made a year later by Nagaoka of Japan. Since mercury has an atomic number of 80 and that of gold is 79, the expulsion of a proton from the mercury atom should form gold or an isotope of gold. These results are not generally accepted; careful repetition of the work has shown that the claims are premature.

Paneth and Peters of Berlin University have recently reported that hydrogen can be transmuted into helium. They condensed some hydrogen on the surface of the metal palladium and converted it into water by burning it off with excess of oxygen. The water was frozen out with liquid air, the excess of oxygen absorbed with cooled charcoal, and the residual gas passed into a small capillary tube fitted with internal electrodes. Paneth and Peters claimed that on passing an electric discharge through the tube they observed the spectrum of helium. They stated that one ten millionth of a cubic centimetre of helium was so formed.

In January, 1926, A. Smits of Holland published the results of some experiments on lead. He reported that this metal could be converted into mercury and thallium by means of a quartz-lead vapour lamp, but so far his results have not been confirmed.

The difficulty of this kind of research is that only minute quantities—if any—of the transmutation products are possible, and the chemical tests employed are so delicate that a slight trace of any impurity in the original substances, or in the vessels used, deceives the experimenter. Thus neon and helium, two reputed products of transmutation, can get into the apparatus from the air, and there is enough lithium in tobacco smoke to give a positive test for this element. The chemical journals in which Ramsay published his work do not tell us whether he smoked during his experiments. It has been seriously suggested that the gold Miethe obtained from mercury actually came from his gold spectacles! At the moment there need be no worry over an economic crisis precipitated by the production of synthetic gold in the laboratories of this or of any other country. If the transmutation of the base metals into gold be possible, it can only be brought about by the liberation of an exceptionally large quantity of energy in a highly concentrated form. Such a transmutation could never be a successful commercial proposition. On the other hand, as Soddy has pointed out, the formation of gold from a heavier element such as lead would liberate such gigantic supplies of atomic energy that the gold would be a by-product; the energy liberated in the process would be far more useful than the gold.

As yet, we cannot build up elements, but remarkable results have been obtained by Rutherford during the last fifteen years on the artificial disintegration of elements. He appears to have produced hydrogen from various elements by bombarding them with α-particles. In conjunction with Chadwick he showed that swiftly moving hydrogen atoms are produced by bombarding nitrogen with α-particles from radium C. The nucleus of the nitrogen atom suffers from the impact of the swiftly moving α-particle and a proton or hydrogen nucleus is ejected with a high velocity. But the number of direct hits registered is very small. Rutherford has calculated that only one α-particle in 300,000 succeeds in getting near enough the nucleus to knock out a proton. Even if the entire α-radiation from a gram of radium were absorbed by nitrogen only ·0000005 c.c. of hydrogen would be produced in a year. This means that we should have to wait over 30 billion years for one cubic inch of hydrogen! Aluminium, oxygen, boron, fluorine, phosphorus and sodium also produce swiftly moving hydrogen atoms when bombarded with α-particles. In addition to hydrogen atoms of mass 1, particles of masses 2, 3, and 4 have been detected. In 1923 Kirsch and Petterson, two Viennese physicists, showed that with improved apparatus swiftly moving protons could be detected when nearly all the elements were bombarded with α-rays. John Dalton's aphorism: "Thou knowest no man can split an atom", is now of purely historical interest.

The new alchemy is as fascinating as the old, although the modern alchemist, unlike his mediæval predecessor, has no illusions concerning the commercial value of his transmutations. He realises that the energy liberated during a transmutation will be of far more value than the transmutation-product. Chemists are impatiently awaiting the time when the vast stores of energy in the radioactive substances can be utilised. At present the emission of energy from these bodies is so slow that it cannot be used profitably. We have said that energy emitted by a pound of uranium will drive a liner across the Atlantic, but the time taken to emit this amount would be five billion years—rather a long time for the tourist or the business man.

One thing however is certain. The machinery of the industrial world cannot always be driven by the extra-atomic forces set free by the combustion of coal and oil; these are gradually disappearing from the earth's crust. Man must find a new source of energy or relapse into a state of barbarism. He must either find some new fuel or utilise the internal energy of the atom. The energy that is the life blood of modern civilisation and that Nature only gives grudgingly is locked up in the very atoms around us. One day man must pick the lock or perish.

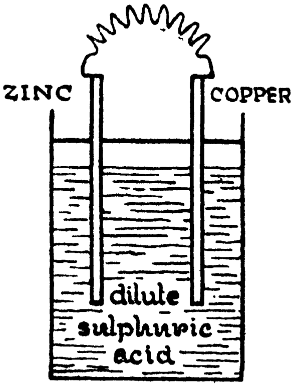
CHAPTER V

CHEMISTRY IN THE SERVICE OF ELECTRICITY

THE word electricity is derived from the Greek *electron*, meaning amber, and it was with this substance that the earliest electrical effects were produced. The ancients knew that amber, when rubbed, possessed the power of attracting light objects. Little advance was made on their knowledge until about A.D. 1600 when Gilbert, physician to Queen Elizabeth, discovered that electricity could be generated by rubbing many substances with silk or fur. In the eighteenth century large machines for producing frictional electricity were constructed, and the effect of the electric discharge on many substances studied. It was found, for example, that an electric current separated mercury and zinc from their oxides and silver from solutions of its compounds. Priestley examined the action of electricity upon such liquids as alcohol and water and he noted the production of hydrogen from the latter. In 1800 Nicholson and Carlisle decomposed water into hydrogen and oxygen by means of electricity.

The electric machines used by these earlier investigators were cumbersome and only gave a small current of high voltage. Although they produced very large sparks, from the point of view of their chemical effects they were not so efficient as the electric cell or battery. We owe the discovery of this to Volta (1808), an investigator whose name is perpetuated in the electrical term volt, the unit of pressure of an electric current. Volta's cell consisted of two plates, one of copper and one of zinc, suspended in dilute sulphuric acid. He found that if the two plates were connected by a wire a current flowed from the copper to the zinc (Fig. 20).

In 1807 Sir Humphry Davy showed that electricity has the power of splitting up a large number of compounds into their constituent elements, provided the compounds are in a molten condition or dissolved in water. Davy isolated the metals sodium and potassium by passing a current of electricity through molten caustic soda and caustic potash. Sodium and potassium are soft silvery-white metals that tarnish in the air immediately, owing to combination with the oxygen. Their affinity for oxygen is so great that they decompose water with extreme violence forming hydrogen and either caustic soda or caustic potash.



VOLTA'S CELL

FIG. 20

If a piece of zinc be placed in sulphuric acid the zinc gradually dissolves with the evolution of heat. If, in addition, a plate of copper be placed in the acid as in Volta's cell and the two plates connected, a current flows. Such an arrangement constitutes a simple battery or cell. But in place of the heat energy obtained in the case of zinc we now get electrical energy. An electric cell or battery is a system in which a chemical action, which would otherwise produce heat, generates electrical energy instead. It can be shown that electrical energy can be used up or produced during chemical change. Energy is liberated or consumed during a chemical reaction, and it may take the form of heat, light, electricity or mechanical motion. These are all different forms of the same thing — energy. Observations by chemists and physicists during the last hundred years have shown that any one form of energy can be transformed into any other form. We know that the forces bringing about any spontaneous natural change can be made to do work. The force of gravitation may be utilised, in the case of falling water, to drive a turbine. The heat generated by the combustion of coal may be made to drive an engine, and this connected to a dynamo will generate electricity. When the current flows through an electric light bulb, heat and light are produced. But what form of energy gives the heat developed by the combustion of coal? If a substance can unite or combine with another it is said to possess chemical or internal energy, and during a chemical change the chemical energy of the system is transformed into an equivalent amount of other energy. In industry and life at least half the chemical changes occurring benefit us by the energy produced rather than by the products of the chemical change. We burn coal and gas to get heat and light energy, not to make carbon dioxide; we want the energy, not the products of combustion. We employ zinc in electric cells, not with the idea of making zinc sulphate or zinc chloride but in order to use the electrical energy produced at the expense of chemical energy. Similarly we do not run electricity into accumulators to make brown lead peroxide, but to store up electricity for future use. Here we store electrical energy as chemical energy, which in turn can be converted back into the former when the accumulator is in use.

The beginning of the nineteenth century witnessed man's successful transformation of chemical into electrical energy, but since the cost of the early electric cells was so prohibitive it excluded any possible industrial applications of electricity. Industry had to wait for Michael Faraday and the dynamo, the production of which was made possible by this English genius. His rise to fame from bottle-washer in Davy's laboratory to the leader of scientific research is one of the most absorbing romances in the history of chemistry. The Prince of Wales in his address before the British Association at Oxford in 1926 said of Faraday:

> Faraday's labours provide one of the most wonderful examples of scientific research leading to enormous industrial development. Upon his discovery of benzene and its structure the great chemical industries of to-day are largely based including, in particular, the dyeing industries. Still wider applications have followed upon his discovery of the laws of electrolysis and of the mechanical generation of electricity. It has been said, with reason, that the two

million workers in Great Britain alone who are dependent upon electrical industries are living on the brain of Faraday; but to his discoveries in the first instance many millions more owe the uses of electricity in lighting, traction, communication and industrial power.

Since the perfection of the dynamo it has been possible to obtain a cheap supply of electricity, especially in regions where the power of running water can be utilised. The power needed to drive the dynamo may come from water-driven turbines, from steam turbines, or from internal combustion engines consuming gas or oil. The world is only on the threshold of electrical development. Cheap water power—the white coal of science—means cheap electrical energy, and countries such as Sweden, America and Canada, are certainly fortunate in possessing almost unlimited supplies of hydraulic power at a very low cost. The future centres of chemical industry will be situated near the world's largest waterfalls. These will be used for generating electricity by means of which aluminium, nitrates, steel, glass, carborundum, carbide and a variety of other substances can be manufactured. The direct production of nitric acid and nitrates from the atmosphere only found a secure footing in Scandinavia and the countries where exceptionally cheap water power is available. Aluminium and calcium carbide are generally made by the help of water-generated electric power, although of course the availability of raw materials determines the mode of generation of the power. It is sometimes cheaper to generate it from fuel in a region where the raw materials are found rather than transport the raw material to another locality where power is cheap.

In the heart of Scandinavia rapid industrial changes are taking place. At Odda, where cheap electrical power is derived from running water, two very large concerns—the Alby United Carbide Factories, Ltd., and the Nitrogen Products and Carbide Company, Ltd.—have come into existence. The source of hydraulic power is the river Tysse which flows into the Sondre Fiord about four miles from Odda, and here are placed the turbines and dynamos by which the power is generated and distributed. The available water makes it possible to obtain 80,000 horse-power. A still larger water-power installation in Southern Norway drains its water supply from the lakes Maarvand, Mosvand and Tinnsjo. The most important power houses are at Rjukan, below Mosvand and above Tinnsjo, and other power houses lower down at Lienfos and Svaelgfos supply the nitrate works at Notodden. In all something like a million horse-power has been harnessed in Norway for generating electrical power and it has been estimated that over 200 million horse-power is available. In the remote Scottish Highlands inexpensive power is produced for the manufacture of aluminium. The British Aluminium Company have utilised the water of Kinlochleven in Argyllshire for this purpose.

What is electricity? Although we know how it works and what it does, we still speculate on its nature. We believe that negative electricity consists of electrons and that these units of negative electricity constitute one of the fundamental bricks that nature uses to build up matter. We also believe that the hydrogen atom is made up from a positive unit of electricity, or proton, and one negative electron. It is now supposed that an electric current is really a movement of electrons through a wire and that the atoms of good conductors of electricity—those of the metals, for example,—have many loosely-held electrons. Why is it that glass when rubbed with silk acquires a positive charge and yet sealing wax when rubbed takes on a negative charge? On the electron theory, some electrons are rubbed off the glass, which consequently takes on a positive charge; the sealing wax, however, attracts electrons from the substance with which it is rubbed, and so becomes negatively charged.

The electron plays a very important part in electro-chemical reactions. If we put two metallic plates into perfectly pure water—an extremely rare product that very few chemists have prepared—and connected the plates to an accumulator or to an electric lighting circuit, we should find that the water failed to conduct electricity. This could be proved by putting a lamp in circuit; it would not light up. If we dissolved sugar, or alcohol, or glycerin in the water, it would still remain a non-conductor of electricity. But if we add a trace of acid, say sulphuric acid, or of an alkali, which has properties opposite to those of acids, or a pinch of common salt, then the water will conduct electricity. All soluble substances could be tested in this way and we should find that they could be classed into two groups: substances which give conducting solutions and those which do not. These are termed *electrolytes* and *non-electrolytes* respectively. Salt is an electrolyte, sugar a non-electrolyte. Acids, alkalies and salts—the compounds formed by the union of acids and alkalies—all form solutions that conduct electricity, that is, they are electrolytes.

When a current of electricity is passed through a solution of an electrolyte, chemical decomposition sets in. Such a decomposition by means of the electric current is called *electrolysis*, which literally means loosening by electricity. If a current be passed through water made slightly acid, the water is split up into the two gases, oxygen and hydrogen, the former being liberated at the *anode*, or positive electrode, and the latter at the *cathode*, or negative electrode. The electrodes are the conducting plates or rods, usually made of metal, that dip into the solution. When a solution of copper sulphate is electrolysed between electrodes of platinum, one of the electrodes, the cathode, becomes coated with a deposit of copper, whilst bubbles of gas, which can be identified with oxygen, escape at the anode. Advantage is taken of this process for electro-plating objects not only with copper, but with other metals such as silver, gold, nickel and chromium.

During electrolysis there is a movement of matter towards the positive and negative electrodes. Faraday, one of the earlier workers on the subject, suggested that the molecules of the dissolved substance are split apart by the energy of the current. This explanation has since proved to be incorrect; in fact none of the energy of the current is used in splitting up the molecules at all. The first satisfactory explanation of electrolysis came from Svante Arrhenius, a Swedish chemist. His theory of electrolytic dissociation, advanced in 1887, assumes that the molecules of an electrolyte break up or ionise spontaneously into charged particles as soon as they come into contact with water. These charged particles are termed *ions*. The ions of the metals and hydrogen, which carry positive charges, are known as *cations*, because being positively charged they are attracted towards the negative electrode or cathode, the ions of the non-metallic elements being negatively charged, are called *anions*. Ions of an element are not the same as the ordinary atoms of the same element. They are atoms which have become positively or negatively charged either by gain or loss of electrons and as charged atoms they have properties differing from those of neutral atoms of the same kind. Thus neutral sodium atoms decompose water readily but positively charged sodium atoms or sodium ions will not. Sodium chloride when dissolved in water immediately splits up or ionises into positively charged sodium ions and negatively charged chlorine ions, which lead an independent existence in the solution.

Acids, alkalies and salts split up in a similar manner when dissolved in water, the metal portion of the salts becoming positively charged, i.e. it becomes a *cation*. When a molecule of an acid undergoes electrolytic dissociation it splits up into a hydrogen ion (cation) and an *anion*, consisting of a negatively charged atom of a non-metal or a negatively charged group of atoms termed a radicle. Hydrochloric acid, for example, ionises in water into positively charged hydrogen ions and negatively charged chlorine ions. Sulphuric acid on the other hand ionises into hydrogen ions and sulphate ions. This can be represented as follows:

$$\underset{\text{hydrochloric acid}}{HCl} \rightleftharpoons \underset{\text{hydrogen ion}}{H^{+}} + \underset{\text{chlorine ion}}{Cl^{1}}$$

$$\underset{\text{sulphuric acid}}{H_2SO_4} \rightleftharpoons \underset{\text{2 hydrogen ions}}{2H^{+}} + \underset{\text{sulphate ion}}{SO_4^{11}}$$

The arrows show that the actions are reversible. In the presence of water ionisation takes place and is assumed to be complete when the substance is dissolved in an infinitely large volume of water. If the water is removed by evaporation the degree of ionisation decreases owing to the combination of ions to form molecules. When an alkali undergoes ionisation it splits up into positively charged metal ions and negatively charged *hydroxyl* ions (OH^{1}). The latter are derived from the group of atoms known as the hydroxyl group. Caustic soda, or sodium hydroxide, ionises as follows:

$$\underset{\text{caustic soda}}{NaOH} \rightleftharpoons \underset{\text{sodium ion}}{Na^{+}} + \underset{\text{hydroxyl ion}}{OH^{1}}$$

It will be observed that the number of charges carried by the ion corresponds to the valency of the element or group of elements from which it is derived. Sodium, valency 1, carries one positive charge; copper, valency 2, carries two positive charges; aluminium, valency 3, carries three positive charges. The solution of an electrolyte must be electrically neutral and consequently the positive charges on the cations are balanced by an equal number of negative charges on the anions.

Accepting the theory of electrolytic dissociation as outlined above, how does it explain the passage of electricity through an electrolyte and the phenomena of electrolysis? A solution of an electrolyte contains free anions and cations. When electrodes are immersed in the solution and a current is passed, the ions move to the electrodes under the influence of the current. The charged ions travel unchanged through the liquid towards the oppositely charged electrodes; the negatively charged anions are attracted towards the positively charged electrode (anode) and the positively charged cations are attracted towards the negatively charged electrode (cathode). Thus when copper sulphate solution is electrolysed, the positively charged copper ion travels to the negatively charged electrode where it liberates its charge by taking two up electrons. The copper ion then becomes a copper atom, which is deposited as metallic copper on the cathode.

$CuSO_4$	$=$	Cu^{++}	$+$	SO_4''
copper sulphate		copper ion		sulphate ion
		$\downarrow$ to cathode		$\downarrow$ to anode
		$Cu^{++} + 2$ electrons $=$ metallic copper		gives up 2 electrons at anode

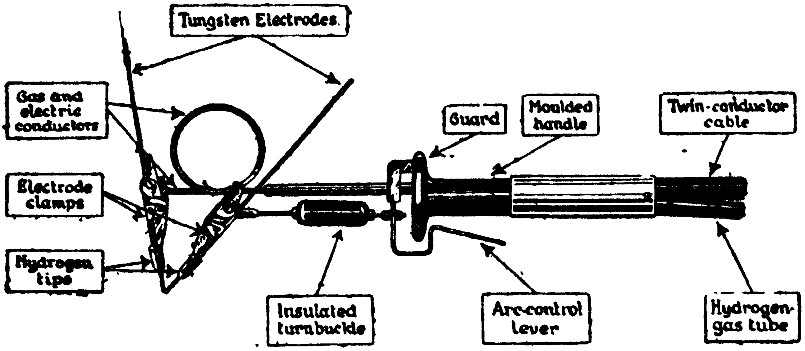
It is the ions that carry the electricity through a solution. Solutions of non-electrolytes, which do not ionise, are therefore non-conductors. Pure water is practically a non-conductor, although it does undergo a very slight ionisation. Only 1 molecule of water in about 550,000,000 is ionised. Tap water is an electrolyte on account of the dissolved impurities present in it. An electrolyte not only conducts electricity when in solution; it also conducts when fused or melted, from which we deduce that electrolytes are dissociated, or split up into ions, when in the fused condition.

The application of electrolysis to chemical industry is comparatively recent. Sir Humphry Davy foreshadowed its use in the preparation of metals early in the nineteenth century, when he prepared the metals potassium, sodium, magnesium and calcium by the electrolysis of their compounds in a molten state. Davy prepared sodium by passing electricity through molten caustic soda contained in a silver dish. A silvery white metal that spontaneously ignited in the air was formed at the cathode. In modern works sodium is still prepared by the electrolysis of fused caustic soda. Magnesium, a metal that has been recently used in the manufacture of light aluminium alloys, is made electrolytically from a mineral termed carnallite, large deposits of which occur in the salt beds at Stassfurt, in Prussian Saxony. Carnallite, a double salt of potassium chloride and magnesium chloride, is melted in an iron crucible, which forms the cathode, a rod of carbon serving as anode. During electrolysis the metal collects at the cathode as a silvery white metal. Before the war Germany was the only country manufacturing magnesium on a commercial scale. The production of the metal during the war was greatly stimulated owing to the use of its alloys in making the metal parts of aeroplanes and airships. As carnallite was not available to this country and her allies other sources of raw material were used. A mixture of magnesia (magnesium oxide) and magnesium chloride was employed instead in many countries. In the process adopted by the Magnesium Co. of Wolverhampton, a specially purified mixture of fused magnesium and sodium chlorides was electrolysed in a cell containing molten lead, which formed an alloy with the magnesium set free during the electrolysis. The lead-magnesium alloy was then decomposed in another cell and the magnesium separated. Calcium is similarly manufactured by the electrolysis of the fused chloride, although the scale of production is small owing to the limited technical applications of the metal. Small quantities of calcium and barium modify the properties of lead, and alloys of these three metals have been extensively used in Germany and America as bearing metals under the names of *Kalzium-metall* and *Ulco* metal. These alloys are formed by the electrolysis of mixtures of the chlorides of the metals between a cathode of molten lead and a carbon anode.

The entire world's production of aluminium is now obtained by electrolysis. For the greater part of a century this metal, now an industrial and domestic necessity, remained a chemical curiosity. In 1854, when Deville obtained the metal by heating aluminium chloride with potassium, it cost more than its weight in gold, and at international exhibitions small bars of it might be seen labelled, "Silver from Clay". At this time a helmet of aluminium was presented to the King of Denmark, a gift that would hardly be appreciated by a present day monarch. Aluminium is a widely distributed element; in fact it forms some 7·3 per cent of the earth's crust. Clay contains a considerable amount of aluminium, although at present it is not commercially profitable to extract the metal from this source. During the war, however, a method was developed in Germany for preparing the metal from kaolin (china clay) or from clays rich in kaolin. The metal was in great demand since its alloys with magnesium were employed for the framework of Zeppelins and aeroplanes. The principal ores of aluminium are bauxite, or aluminium oxide, vast deposits of which have been found in nearly every continent, and cryolite, a mineral that is indispensable in the present electrolytic preparation of the metal. The present method resulted from a discovery of Héroult and Hall in the 'eighties, that molten cryolite dissolves alumina (aluminium oxide), and that this forms the best electrolyte for the preparation of the metal. Héroult alighted on his discovery accidentally; Hall, working on his own with home-made apparatus, discovered a process that chemists had been looking for over a period of fifty years.

In Hall's process, purified alumina obtained from bauxite is dissolved in molten cryolite and the mixture electrolysed at a temperature of about 1,000° C. in a specially constructed iron vessel lined with carbon, which acts as the cathode. The anode consists of a series of carbon rods held in position by copper clamps. An electric arc is produced between the carbon anodes and the carbon lining of the vessel, the heat produced being sufficient to melt the cryolite. Then the carbon anodes are raised slightly, the purified alumina tipped in, and the surface of the molten mass covered with coal. The aluminium ions travel to the cathode during the electrolysis, liberate their positive charge and become atoms of aluminium. Molten aluminium is withdrawn periodically from the floor of the electrolytic cell. A cell of dimensions 5′ × 3′ × 1′ produces about 177 lbs. of aluminium per day. Specially purified aluminium for metallurgical purposes is prepared by alloying the metal with copper and then electrolysing the alloy under fused cryolite.

Another valuable product of electrolysis is caustic soda, a chemical that is widely employed in nearly every industry. Large quantities of it are used in the manufacture of soap, paper, glass, artificial silk and bleaching materials; it is also used in the dyeing industry and in the refining of oils. Caustic soda is prepared by the electrolysis of common salt (sodium chloride) either in solution or in the fused state. In the Castner-Kellner process the sodium chloride solution is electrolysed in a cell divided into three compartments by partitions which reach nearly but not quite to the floor. A layer of mercury on the floor of the cell separates one compartment from another. The middle compartment, into which dip a number of iron rods forming the cathode, contains water, while the two outer compartments, which contain the anodes, are filled with strong salt solution. When the current is passed the chlorine ions pass to the anodes, where they liberate their negative charge and form ordinary gaseous chlorine; this is led away and compressed. The sodium ions travel towards the iron cathode in the middle cell, but they are trapped by the layer of mercury with which they form an alloy or amalgam. By rocking the cell the mercury and sodium alloy flows backwards and forwards and when it enters the middle compartment it reacts with the water there, forming a solution of caustic soda and hydrogen gas, which comes off at the cathode and is pumped into cylinders. In another process for the manufacture of caustic soda the salt solution is electrolysed in a cell fitted with a diaphragm, so that the sodium and chlorine cannot react with one another. In some factories caustic soda is made by the electrolysis not of salt solution but of fused salt, molten lead being used as a cathode. The sodium liberated during electrolysis forms an alloy with the lead, and this is decomposed by steam into caustic soda and hydrogen.


Tungsten Electrodes
Gas and electric conductors
Electrode clamps
Hydrogen tips
Insulated turnbuckle
Guard
Moulded handle
Arc-control lever
Twin-conductor cable
Hydrogen-gas tube

The ATOMIC HYDROGEN ARC WELDING TORCH.

FIG. 21

Hydrogen and chlorine are important by-products in the manufacture of caustic soda. Hydrogen is used for the preparation of synthetic ammonia and quick-drying varnishes, and for the conversion of liquid fats into solid, edible fats. The flame of hydrogen burning in oxygen is known as the oxy-hydrogen blowpipe flame. It is used in cutting and welding metals. Langmuir, of the General Electric Company, has shown that ordinary gaseous hydrogen (H_2) splits into up atomic hydrogen (H) when strongly heated in contact with an electrically heated tungsten wire. The same chemist has shown that this form of hydrogen, which is chemically very active, is also produced when an electric arc between tungsten electrodes is allowed to burn in hydrogen at atmospheric pressure. When the atoms of hydrogen (H) re-combine to form molecules (H_2) much heat is liberated and use is made of this in the atomic hydrogen arc welding torch. A jet of hydrogen is blown through an electric arc between tungsten electrodes. (*Plate* 11.) Atomic hydrogen is formed by the breaking up of the hydrogen molecules, and the atoms formed re-combine immediately beyond the arc with the evolution of much heat. The heat produced by the change of one cubic foot of hydrogen from the atomic to the molecular condition produces about 130,000 calories, or enough heat to boil nearly three pints of water. The atomic hydrogen torch will melt tungsten (melting point 3,400° C.), and the high temperatures obtainable with it make it particularly suitable for welding refractory metals.

Chlorine, which was used during the war as a poison gas, has been put to a more humane use in sterilising drinking water. Some seventy-five per cent of the drinking water in America is now sterilised by means of it, with the result that the death rate from typhoid has dropped considerably. It is employed in the purification of sewage, and both chlorine and its compounds are used for the bleaching of wood pulp in the manufacture of paper and artificial silk, and also for bleaching flour. Liquid chlorine is used for the extraction of metals, especially gold, and for the refining of crude natural oils. It also finds employment in the manufacture of dyestuffs, insecticides, fire extinguishing liquids, grease-removers, solvents for organic substances, chloroform and drugs. When chlorine was discovered by the Swedish chemist Scheele in 1774 it remained for years a chemical curiosity. Now it is a necessity.

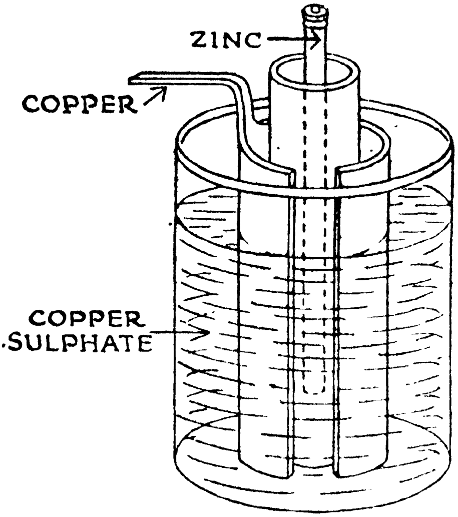
If the electrolysis of sodium chloride solution is carried out in a cell so that the products of electrolysis can mix, the chlorine reacts with the caustic soda formed at the cathode and forms sodium hypochlorite. This is extensively used as a bleaching agent and antiseptic. It is the essential constituent of the Carrel-Dakin solution, a very effective germicide, and of the well-known antiseptic called Milton.

Many articles are coated with copper and other metals by electrolytic methods. This is known as electro-plating. If a solution of copper sulphate is electrolysed between two copper electrodes, the copper ions, formed from the copper sulphate, travel to the cathode, which gradually becomes coated with metallic copper, and the sulphate ions travel to the copper anode and attack it to re-form copper sulphate. The net result is that the amount of copper sulphate in solution remains constant, but copper is transferred by the current from the anode to the cathode. In the process of electro-plating a rod of pure copper forms the anode and the object to be plated is the cathode. By the electrolysis of solutions of their salts the metals gold, silver, nickel and chromium can be deposited on cheaper metals. In the case of silver and gold, solutions of sodium silver cyanide and sodium gold cyanide respectively are employed as the electrolytes and the object to be coated, if non-metallic, is covered with a layer of graphite—the so-called black-lead put in pencils—to make it conduct the current. For nickel-plating, nickel sulphate in dilute citric acid is used. (*Plate* 12.) Chromium-plating on iron and steel is done by electrolysing a solution of chromium sulphate containing chromic acid, the object to be plated forming the cathode. (*Plate* 13.) In the manufacture of the best chromium plate the iron or steel receives a preliminary coating of nickel. It is also possible to deposit alloys of metals by electrolysis.

Copper tubes and pipes have been prepared by the electrodeposition of copper on rotating cylinders and it has been claimed that such tubes are superior to those formed by brazing. Galvano-plastics can be made by depositing copper on objects made of plaster, wax, wood or gutta-percha, which are previously coated with a conducting layer of graphite. In a similar manner electrotypes of plates and engravings are prepared by pressing the original plate into wax, or soft metal, and then coating the mould thus formed with metal by making it the cathode of a plating solution. The metal shell formed by electro-plating is stripped from the wax mould and backed up with metal. Master gramophone records can be copied from the original wax discs by an application of this method.

Many metals are now refined by electrolytic methods. Copper is refined by the electrolysis of copper sulphate solution between a plate of impure copper, which forms the anode, and a cathode of very thin, pure copper plate. During electrolysis crude copper is dissolved off the anode and pure copper is deposited on the cathode, from which it can be readily removed. The impurities in the original copper either go into solution or else sink to the bottom of the electrolytic bath as anode slime or mud, which is of great value. That obtained from copper refineries is worked up for the extraction of gold and silver. Metal containing some ninety per cent of silver can be obtained from the anode slimes of copper works. Silver, gold, zinc, nickel and iron are refined by electrolysis.

The widespread application of electricity to chemical industry has only been made possible by the dynamo, which has superseded the voltaic cell as a source of electricity for industrial purposes. We have examined the simplest voltaic cell—a strip of copper and of zinc immersed in a vessel containing dilute sulphuric acid. A cell does not generate electrical energy. The electric charges are present in the elements of the substances forming the cell as electrons and these electrons are taken up or removed from atoms to form ions. When the electrons detach themselves from one atom and attach themselves to another they move along the connecting wire of the cell; in other words we say that a current moves through the wire. This electrical energy, which is derived from the chemical energy of the components of the cell, can be converted into mechanical energy, e.g. it will drive a motor.



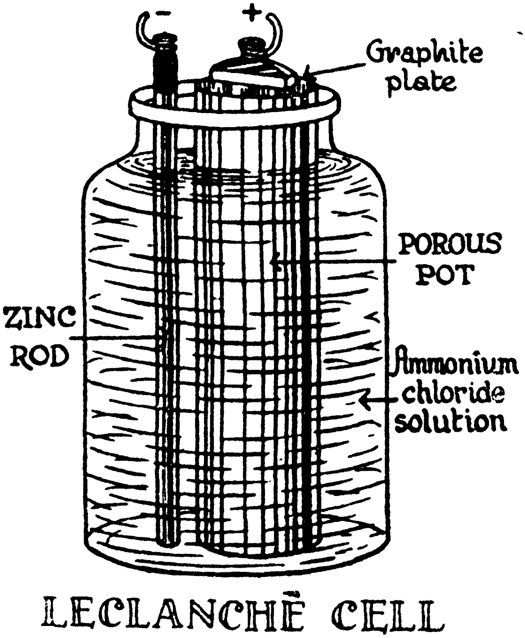
DANIELL CELL

FIG. 22

Volta's cell has several disadvantages. Its electromotive force (E.M.F.) or voltage soon drops during use and the copper plate becomes rapidly corroded. Improvements have been made by substituting carbon rods for copper, and by amalgamating the zinc plate with mercury, which protects the zinc. These carbon electrode cells rapidly lose their power owing to bubbles of hydrogen covering the carbon, causing what is termed polarisation. This trouble can be eliminated by adding to the cell a substance that combines with or oxidises the hydrogen; potassium dichromate and manganese dioxide have been used for this purpose. The Daniell cell consists of a zinc electrode immersed in a solution of zinc sulphate in dilute sulphuric acid, and a copper electrode immersed in a solution of copper sulphate, the two solutions being kept apart by means of a porous pot (Fig. 22). A current flows from the copper to the zinc when the two electrodes are connected by a wire, and an examination of the contents of the cell after it has run some time would reveal that zinc has disappeared from the zinc rod and formed zinc sulphate and that copper has been deposited on the copper plate from the copper sulphate solution. The reaction which occurs in the cell may be expressed by the equation:—

Zinc + copper sulphate = zinc sulphate + copper.

Two negative electrons are given up by the zinc atom to form a zinc ion which goes into solution and the two electrons pass round the conductor wire to the copper electrode where a copper ion receives them and is converted into a neutral copper



LECLANCHÉ CELL

FIG. 23

atom, which is deposited on the copper electrode. Chemical energy is converted into electrical energy.

The Leclanché cell (Fig. 23), used for electric bells and private telephones, consists of a solution of ammonium chloride (sal ammoniac) in which are immersed a zinc rod (anode) and a plate of graphite (cathode). The latter is packed in a porous pot with manganese dioxide and crushed carbon to act as a depolariser, i.e. to remove the hydrogen that would be formed on the carbon during the running of the cell. The power of this cell falls during use but it is regained on standing. It is thus only suitable for intermittent use. In a dry cell (Fig. 24) a cylinder of zinc, which forms the anode, is filled with ammonium chloride and ground carbon made into a porous paste with paper pulp, sawdust and glycerin. A carbon rod in the centre of the porous mass forms the cathode. Dry cells are used for door bells, electric torches, and telephones, and in wireless sets and cars.

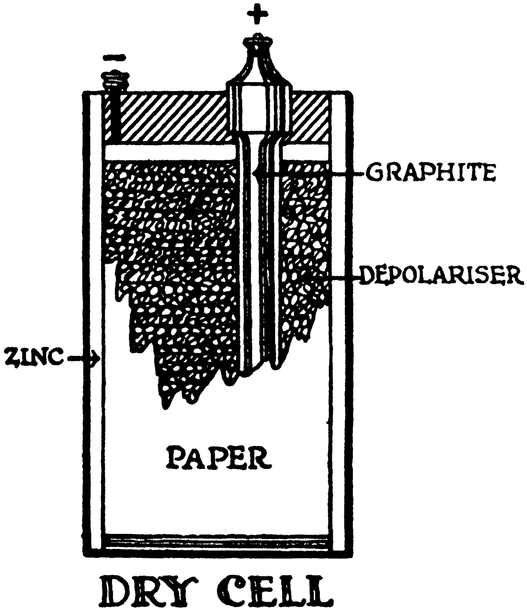


FIG. 24

Another cell that has been successfully developed in Germany and America is known as the cupron element, the electrodes of which consist of zinc and copper, the latter being coated with a film of copper oxide. Both electrodes are suspended in an electrolyte of strong caustic potash solution (30–40 per cent). When the cell is running the zinc dissolves in the caustic potash, while an equivalent amount of the copper oxide is converted into copper. When all the copper oxide has been changed to metal, the latter can be heated in air to reform copper oxide. The cupron cell possesses the advantages of containing only one liquid, of not deteriorating with use and of requiring no diaphragm as in the Daniell cell.

Cells in which an electric current is derived from the chemical changes that take place in them are known as primary cells. These have been largely replaced by secondary or storage cells, which are charged by means of an electric current derived from a dynamo. This supplies energy to the cell, which during use gives a certain portion of the energy back, about 15 per cent being lost over a discharge period of from ten to twelve hours. A common form of secondary cell is the lead accumulator. This consists of two plates of lead immersed in dilute sulphuric acid, one of the plates containing perforations filled in with brown oxide of lead (lead dioxide). On connecting the plates by a wire a current flows from the lead peroxide plate to the lead plate as the cell is discharged. The chemical energy stored in the cell is transformed into electrical energy, and when the chemical reaction that occurs is complete the cell is run down or discharged. In this condition it no longer delivers current. But the cell can be recharged by passing an electric current from a dynamo in the opposite direction to that of the current given by the cell. The result is that electrical energy is converted into chemical energy, which is stored until wanted. During discharge the lead and brown oxide of lead react with the sulphuric acid to form lead sulphate and water. This process is reversed when the cell is charged up, that is, sulphuric acid, lead and brown lead oxide are regenerated. This can be represented:—

$$\text{Lead oxide}+\text{lead}+\text{sulphuric acid} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \text{lead sulphate}+\text{water}$$

One objection to the use of the lead accumulator is that the lead makes it heavy for transport. Researches have therefore been made on the possibility of using other metals. Lead-antimony alloys have been employed instead and these, being harder than lead, can be formed into thinner plates. The

Edison accumulator, a serious competitor of the lead cell, consists of plates of finely divided iron and nickel hydroxide in a solution of caustic potash. The first cost of this accumulator is high, owing to the expensive nickel and to complexities in construction, but this is compensated by the fact that the accumulator is mechanically strong and stands rough handling.

Storage cells have a number of uses. Many factories close down at night, but since it is not advisable to shut off the steam power completely—the boiler fires must be kept alight—dynamos are kept running to charge up storage cells for use in the daytime at peak periods when the power consumption is high. Storage cells are used in portable lamps, for wireless purposes, for driving cars and for motor ignition.

It is well known that heat is produced when electricity passes through a solid conductor, and given suitable conditions the temperature may be raised until the conductor melts or vaporises. If current is supplied to two carbon rods in contact and the rods then separated a short distance an electric arc is produced. Electrical energy is transformed into heat energy and by this means temperatures in the region of 3,000° C. can be obtained; this is sufficient to melt all known metals and to volatilise carbon and lime. By putting a pressure of twenty atmospheres on the arc light temperatures can be obtained rivalling those on the sun itself. In the electric arc a temperature of 6,000° C. is possible. Electric furnaces are arc lights on a very large scale. They consist of powerful arcs produced between carbon electrodes situated immediately above the substance to be heated, the whole being surrounded by a casing of heat-resisting material. The electric furnace was first employed on a large scale by the Cowles Electric Smelting and Aluminium Company at Cleveland in 1885, with Niagara as a source of hydro-electric power.

Calcium carbide, one of the first substances to be made in the electric furnace, is manufactured by passing a current through a mixture of small pieces of coke and lime. The white hot carbide, formed at a temperature of 3,500° C., is run out at the bottom of the furnace into cast iron moulds, where it solidifies. It is used in the manufacture of acetylene and nitrolime (p. 203).

Silicon carbide, or carborundum, another electric furnace product, was first manufactured at Niagara by Acheson, a graduate of Edison's laboratory. The furnace used is built of bricks put together without mortar or cement so that the gases produced can readily escape. It has to be pulled down and rebuilt each time it is charged. The charge consists of coke, which serves as a source of carbon, sand (silicon oxide) to supply the element silicon, and a mixture of sawdust and salt. This is packed into the furnace, a brick structure fifteen feet long and seven feet wide and deep, with carbon electrodes at the end. At the high temperature produced some of the carbon of the coke combines with the oxygen of the silicon oxide, and the silicon formed combines with excess carbon to form carborundum. Since the hardness of this approximates to that of the diamond, it is extensively employed as an abrasive and grinding material. Not only is it used in making grindstones, but for polishing teeth and for incorporation with concrete for pavements and stairs. Owing to its refractory nature, i.e. it can withstand very high temperatures, it is used as a heat-resisting lining for furnace walls. About 30,000 tons of carborundum are produced annually. By heating sand with twice its weight of coal in the electric furnace *siloxicon* or carborundum sand is formed. When mixed with fire-clay this is also used for furnace linings; it is indifferent even to molten iron. ***Alundum***, a form of aluminium oxide, is another valuable abrasive and refractory material. It is produced by fusing purified bauxite in the electric furnace. Zirconium oxide, a by-product of the gas-mantle industry, also finds employment in the manufacture of fire-resisting crucibles, and as *zirkite* is used as a lining for electric furnaces.

The discovery of artificial graphite resulted from the manufacture of carborundum. Large quantities of graphite are manufactured at Niagara by a process due to Acheson. Three tons of powdered coke or anthracite coal mixed with a little sand and pitch are heated in an Acheson electric furnace, the bottom of which is covered with a layer of sand. After twenty-four to thirty hours at 3,000° C. the coke is converted into graphite. To obtain shaped graphite articles such as rods, plates, etc., finely ground coke is mixed with a little iron oxide and after being made into a paste with pitch, the mixture is moulded under high pressure and heated in the electric furnace.

Graphite is used in pencils, for electrical purposes and as a lubricant for machinery where oil is inadmissible owing to high temperatures. A suspension of graphite in a solution of tannin is known as *aquadag*, and this when filtered through rubber and mixed with lubricating oil forms *oildag*. Both are widely used as lubricants.

Graphite, charcoal and diamond are different modifications or varieties of the element carbon; a diamond is crystalline carbon. Moissan prepared artificial diamonds, physically and chemically identical with the natural product, by means of the electric furnace. He made pure carbon by heating sugar, and then heated up the carbon with iron in an electric furnace. When the iron melted it dissolved the carbon, and by cooling the molten iron rapidly the carbon crystallised out in the form of very small diamonds, which were obtained after the iron had been dissolved away with acid. Commercially these diamonds were worthless owing to their small size. Even if large diamonds could be made synthetically the maker would not reap the benefit as the price would drop at once. The price of diamonds remains high because the output is limited by a combine, and because they are highly prized as jewels. The value of a diamond depends upon the price the purchaser wishes to pay for it and not upon its usefulness. Small diamonds are used in grindstones and drills, although for this purpose they can be quite satisfactorily replaced by carborundum and other abrasives.

Fused silica ware (silicon dioxide) is now manufactured in the electric furnace. Pure silver sand is fused by a current passing through carbon resistance rods embedded in the sand which flows readily at 2,000° C. When sufficient sand has fused on the resistance rod, the molten substance can be blown and moulded into the required shape. Silica ware stands changes of temperature—a red hot silica crucible can be quenched in cold water without cracking—and for this reason it is used in making chemical laboratory apparatus. *Pyrex* glass, which contains eighty per cent silica, has to some extent replaced baking dishes in the household; food can be cooked and baked in vessels of this new glassware owing to its ability to withstand changes of temperature without cracking. *Vitreosil* is a translucent variety of silica ware.

Large quantities of phosphorus are made by heating carbon, sand and calcined bones—mainly calcium phosphate—in an electric furnace. The phosphorus distils out at the top of the furnace and the calcium of the calcium phosphate forms a liquid slag which is withdrawn from the bottom. Phosphorus is mainly used for making matches and vermin destroyers, and for hardening metals (phosphor bronze). It is convenient at this point to discredit the legend that the phosphorescence of fish is due to phosphorus, and that since they contain much of this element they are good for the brain. Phosphorus was once considered to be good for the brain because a small quantity of it is found in this part of the body! It is true that phosphorus is present in fish; but principally as calcium phosphate in their bones. There is still a widespread belief that brain-power is dependent upon foods rich in phosphorus. There used to be a maxim in the 'sixties in Germany: *Ohne Phosphor, kein Gedanke* (without phosphorus, no thought); and the biologist, Louis Agassiz, is stated to have said that "fishermen are more intelligent than farmers, because they eat so much fish, which contains so much phosphorus". The truth is that besides phosphorus, there are also many other elements in the brain, and there is no valid reason for believing that phosphorus plays a more important part than the rest of the elements.

The electric furnace finds many applications in the metallurgical industries. It is employed for the production of steel and its alloys and for a large number of rare and refractory metals that were chemical curiosities before the age of electricity. Where power is cheap, pig iron is made by heating iron ore, coke and limestone in the electric furnace. Special high quality steels are made in electric furnaces. The charge, which consists of pig iron, steel scrap, iron ore and lime, is heated by a current of 4,000 ampères at 120 volts, carried by large stout carbon electrodes six feet long. Most of the impurities form a slag on the surface of the molten steel, but some remain in the latter and these, consisting chiefly of phosphorus and sulphur, are oxidised away by an air blast. After pouring off the slag the steel is treated with small amounts of special alloys containing carbon and certain metals such as manganese, tungsten and chromium, and the molten steel run out. The electric furnace has also made possible the production of many ferro-alloys, or alloys of iron with other metals. (*Plate* 14.)

CHAPTER VI

METALS AND ALLOYS

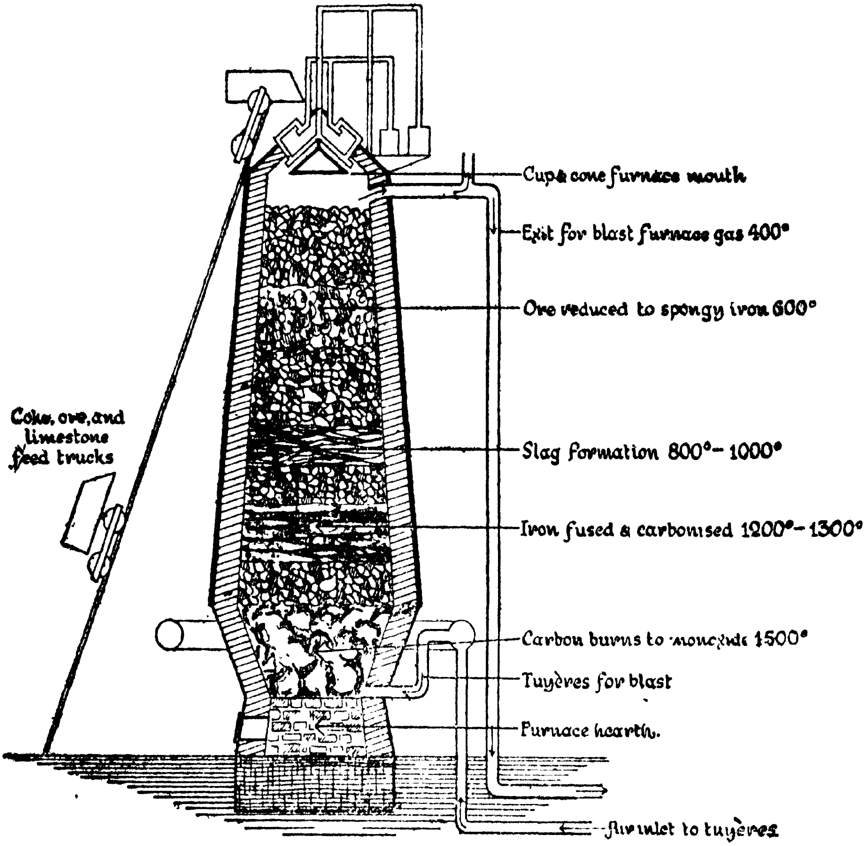
ALTHOUGH metals play an important part in our civilisation, archæology tells us that man once fashioned his tools and weapons of stone. The Stone Age was followed by the Bronze and Iron Ages, and at the beginning of the Christian era about seven metals were employed. The primitive metallurgist could only utilise those metals that occurred free in nature, and since iron is nearly always found in the combined condition this metal was not one of the first known to man. It is quite possible that gold, which is found in many localities in the native or uncombined state, was one of the first metals to be known. The beauty of the metal, and the ease with which it can be worked, must have appealed to primitive man. Silver and copper also occur native, and it is supposed that copper was worked before iron; the Bronze Age began in Greece about 5,000 years ago, and the Iron Age nearly a thousand years later. In Egypt, India and China iron was worked nearly six thousand years ago. Since native metals are scarce, stone tools remained in use until man found out how to prepare metals from ores by smelting. Copper was used before iron, no doubt on account of the greater ease with which its ores are smelted and on account of its malleability; the smelting of iron requires a much higher temperature. Man soon found that the addition of tin to copper hardened the metal and made it more suitable for tools and weapons. This heralded the approach of the Bronze Age. Iron finally took the place of copper and for the last six thousand years has been man's most useful metal. In fact the success of modern nations, in both peace and war, can be measured by their iron output. In the fourth chapter of Genesis reference is made to Tubal-cain as an instructor of workers in iron and brass (copper). It is most likely that iron was first used in India. The Greeks obtained their supplies of iron ore from the coast of the Black Sea and the Romans from Spain and Elba.

Pure iron is almost a chemical rarity—a soft, ductile, silvery-white metal. Industrial iron always contains small amounts of other metals as well as carbon to strengthen and toughen it. It is a widely distributed element, constituting about four and a half per cent of the earth's crust, and besides being the most useful metal of material civilisation it is a necessary constituent of the food and blood of animals, and indispensable to plant life in the formation of chlorophyll, the colouring matter of the green parts of plants. It is the iron of our blood that serves as a vehicle for the transport of oxygen from cell to cell in our body. Haemoglobin, the red pigment of the blood, contains about a half per cent of iron. In cases of anaemia iron is administered in the form of organic compounds, although the best cure for anaemia is said to be liver, which is rich in iron.

The chief ores of iron are the carbonate and oxide of the metal, and these readily yield iron on smelting with carbon or charcoal; until coal came into use charcoal, obtained by burning wood in a limited supply of air, was used in the smelting of ores. The first iron tools were not made from smelted iron ore, but from small pieces of the native metal hammered together. Considerable masses of free iron are still found in Greenland, where the inhabitants shape the metal by hammering. Iron was no doubt first produced from its ores by accident, the most likely suggestion being that pieces of iron ore were used in place of stones in making charcoal or wood fire; the hot charcoal would reduce the ore to the metal especially if a strong wind were blowing to raise the temperature of the fire.

The principal ores of iron are *haematite* (Fe_2O_3), which imparts a red colour to many soils and certain rocks, *magnetite* (Fe_3O_4), *limonite*, or brown haematite, and spathic iron ore (iron carbonate). Limonite consists of iron oxide chemically combined with water ($2Fe_2O_3.3H_2O$). Large deposits of these ores occur in a relatively pure state, and in England the coal that is used for smelting is often found in the same locality, so that much iron ore is smelted at the mine-mouth. There are large deposits of iron in North America, chiefly in Minnesota, Michigan and Alabama, and huge untouched reserves in Brazil which are too far inland to export. The Lorraine deposits, near the Franco-German frontier, produce about 36 per cent of the world's pig iron. Before the war U.S.A. and Germany produced most of the world's iron. In 1500 the world production was 50,000 tons; the latest figures available for the annual production of iron are round about 84,000,000 tons, a figure that does not include steel. About 100,000,000 tons of steel are produced annually. Will our supplies of iron ever be exhausted if they are being used up at such a rapid rate? This problem has occupied the minds of many geologists, and industrialists. Conservative estimates suggest that thirty billion tons of iron ore will be available for the next two hundred years, and after that man must use other metals. It is quite possible of course that one day he will find a method of winning iron from sources that are at present not profitable to the industrialist.

After the iron ore is mined it is screened, i.e. concentrated by removal of earthy matter, a process that may be accomplished either by sifting or by washing. The ore is then roasted to drive off any water present and to convert the iron compounds into iron oxide. It is then smelted with coke and limestone in a blast furnace, a tall iron tower bound with steel plates and lined with fire-resisting brick. The furnace is charged from the top by a cone and hopper arrangement (Fig. 25), and fresh charges are run in as fast as iron and slag flow away at the bottom. About eight feet above the bottom of the furnace are a series of tubes termed *tuyères* ("twyers") through which hot air is blown into the blast furnace. This hot air converts the carbon in the coke into carbon monoxide, which in turn reduces the iron oxide of the ore to iron; this sinks to the bottom of the furnace, and on it floats the molten slag, consisting of the impurities present in the ore combined with the lime formed by the action of heat on the limestone. The slag is mainly calcium aluminium silicate, since aluminium and silicon are the principal impurities in the ore. Phosphorus and sulphur, two undesirable elements that render iron brittle, are also largely removed in the slag. The molten iron is withdrawn from the bottom of the furnace about five to six times daily, and run into moulds where it solidifies as pig iron or cast iron. This is very impure, containing sometimes over


Cup & cone furnace mouth
Exit for blast furnace gas 400°
Ore reduced to spongy iron 600°
Coke, ore, and limestone feed trucks
Slag formation 800°–1000°
Iron fused & carbonised 1200°–1300°
Carbon burns to monoxide 1500°
Tuyères for blast
Furnace hearth.
Air inlet to tuyères

BLAST FURNACE

FIG. 25 [From Partington's *Everyday Chemistry*.

4 per cent of carbon, and 1 to 2 per cent of silicon and other elements, such as phosphorus and sulphur. The slag, which is tapped off through a pipe above the molten iron, is used in the manufacture of Portland cement, and since it contains phosphorus and potash it is also valuable as a fertiliser (basic slag). When Portland cement is mixed with water it sets to a hard mass, even under water, and is therefore useful for engineering work in harbours and rivers.

The gases that pass out of the top of the blast furnace are combustible and hence valuable as fuel. When deprived of suspended dust they are used in internal combustion engines, for heating the air passing in the tuyères of the blast furnace, and also for heating the air blast in the Bessemer steel converter (p. 122). This effects a considerable saving of fuel. The dust which settles contains appreciable quantities of potash and can be employed as a fertiliser.

Tremendous quantities of iron are dealt with in these furnaces. A single furnace will average 750 tons of iron a day, consuming 1,400 tons of ore, 720 tons of coke and 360 tons of limestone, and producing 410 tons of slag and 4,200 tons of combustible gas. The furnaces are constantly recharged day and night until they are worn out. Their efficiency is increased by removing moisture from the air before it passes into the tuyères.

Pig iron contains too many impurities to be of constructional value; they make it very brittle. It contains about 93 per cent of iron, 3 to 4 per cent of carbon, from ·5 to 4 per cent of silicon, and from ·5 to 1 per cent of manganese, which minimises the harmful effects of sulphur. This element, which is always present in small amounts, makes pig iron brittle, and for this reason it cannot be welded. Phosphorus can be largely eliminated by mixing lime with the limestone used in the smelting; the basic slag formed contains the phosphorus. Wrought iron, or malleable iron, is made from pig iron by burning away the impurities until these do not exceed a half per cent. This process, known as puddling, was invented by Cort in 1784, and is carried out by heating the pig iron on the hearth of a reverberatory furnace lined with haematite, or oxide of iron. In a reverberatory furnace the substance is heated by hot gases passing over it. The impurities are oxidised by the oxygen of the haematite and pass into the slag, which is separated from the pasty mass of wrought iron. This is beaten under steam hammers to press out all the slag, and the iron rolled into bars. A new process for the preparation of pure iron was introduced into America in 1927. The iron is produced from pig iron treated in a Bessemer converter (p. 122); the molten liquid is poured into a pool of synthetic slag, and the spongy mass of iron resulting is squeezed and rolled. Wrought iron, which is tougher than steel, can be readily welded. It is used in the manufacture of sheet iron, boiler stays, iron piping, chain-cable and articles that could not be made from brittle cast-iron. Pure iron is too soft for most purposes, but when alloyed with carbon and suitable metals exceptionally hard steels can be produced. Steel is essentially a mixture of iron and iron carbide, or cementite.

Before 1870 cast and wrought iron were used in preference to steel for constructional purposes owing to the high price of the latter. A demand existed for cheap steel; this was satisfied by the introduction of Bessemer's process, which is still used in America and on the continent, although it has been largely replaced in this country by the Siemens-Martin or open-hearth process. In Bessemer's process, the molten pig iron from the blast furnace is run into a converter, a cylindrical steel vessel about 20 feet high and 10 feet in diameter, lined with heat-resisting brick (Fig. 26). The blast of air, which enters through the perforated bottom of the converter, oxidises away the impurities, and these burn with a yellow flame at the mouth of the converter. Phosphorus is removed by lining the

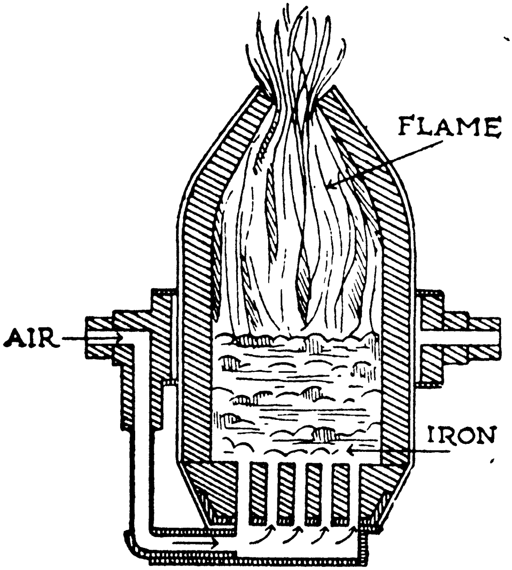


Diagram of
BESSEMER CONVERTER

FIG. 26 [From Partington's *Everyday Chemistry*.

converter with a mixture of lime and magnesia (formed by heating the naturally occurring mineral, dolomite), which absorb the oxidised phosphorus to form basic slag, or Thomas slag. This is a valuable fertiliser. Whilst the iron is still molten, the blast is stopped, and an alloy of iron-manganese containing carbon is added. The steel formed is poured into moulds, and the cast steel annealed in furnaces heated by gas from the blast furnaces.

Before the advent of the Bessemer process, steel was made by heating wrought iron bars packed in charcoal to a red heat for several days. Under these conditions iron takes up a small amount of charcoal to form steel. The best steel for fine tools and cutlery is still made by heating wrought iron bars with charcoal for one or two weeks. Owing to the formation of blisters on the surface of the steel it is known as blister steel, and this when fused in graphite crucibles forms cast steel, or crucible steel.

Steel is generally made in this country by the Siemens-Martin open hearth process. A mixture of scrap iron, cast iron and the requisite amount of haematite (iron oxide) is heated on an open hearth by combustible gases from the blast furnaces, or by the gases formed by passing air over red-hot coke. If the iron ore contains phosphorus the hearth is lined with ganister (silica rock) or with a mixture of lime and magnesia The molten steel is run off by tilting the hearth. More steel can be produced at a time by the open hearth process than by the Bessemer process, and it has the advantage over the latter in that it can be more easily controlled. By varying the proportions of cast iron and haematite, steels of different carbon content may be obtained. Soft steel contains between ·08 and ·18 per cent of carbon; structural steel, which must be strong and easily machined, contains from ·15 to ·25 per cent; medium hard steel for large forgings, car axles and locomotives requires from ·65 to ·85 per cent; hard steel for tools and rock drills contains from 1 to 1·2 per cent carbon. Carbon increases the strength of steel. A process for hardening alloy steels, known as "nitrogen hardening", was perfected in 1926 by Dr. Fry, of Krupp's metal works, and it has been widely used for hardening steel parts requiring high strength, toughness, and durability. The steel is hardened at a low temperature in ammonia gas. Special high quality steels are made in the electric furnace in which a much higher temperature can be obtained than in the blast furnace. (*Plate* 15.) Where power is cheap the smelting of iron ore is sometimes done electrically. The electric furnace is specially suitable for the production of alloy steels of high melting point.

The properties of steel depend upon the amount of carbon it contains and upon its temper. With increasing amounts of carbon the tensile strength of the steel increases, but the ductility, or ability to be drawn, decreases. If steel is heated to a high temperature and cooled in cold water or oil it becomes as hard and brittle as glass. It is known as quenched steel, and when this is heated gradually it loses its hardness but becomes tougher, the amount of change depending on the temperature to which it has been subjected. The process is called *tempering*, and the temperature to which the steel is heated can be roughly determined from the colour of the thin film of oxide on the surface of the steel. This colour may vary from yellow through brown to blue. Steel for razor blades is tempered yellow; that for springs, chisels and saws is tempered blue. When hot steel is quenched, reheated to 875°, and then allowed to anneal or cool slowly, a hard, but not brittle steel is obtained.

Wrought iron is case-hardened by heating in contact with carbon, whereby a film of steel is formed on the surface of the iron. (*Plate* 16.) In this way the properties of a hard steel surface are combined with the tough body of mild steel. Armour plate is made by case-hardening soft steel plates on one side and cooling with cold water. A shell makes a clean hole in armour plate whereas ordinary hard steel splinters.

During the present century many special steel alloys have come into use. Before 1910 alloy steels were chiefly used in the manufacture of big guns, armour plate and projectiles, but now they are used in all the metal working industries. The effect of adding other substances to steel has been thoroughly investigated since the pioneer work of Sir Robert Hadfield, who in 1888 examined the effect of manganese on the strength of steel. Manganese steel is of great value; manganese is, in fact, added to nearly all steel. Hadfield's steel, containing from 9 to 14 per cent of manganese, is very tough and withstands a good deal of heavy mechanical shock. It is used for rock crushing machinery, steel rails and safes. During the war steel helmets and breast-plates were made from it. Hadfield also discovered that the addition of silicon to steel destroys its magnetic properties, and silicon steel is hence employed in the manufacture of electro-magnetic and electrical transformers. Ferro-silicon, an alloy of iron and silicon, is added to pig-iron in the manufacture of good grade cast-iron. An excellent steel for cutting tools contains 1·28 per cent silicon, 1·2 per cent carbon and ·91 per cent of manganese. Aluminium has been proposed in place of silicon for the manufacture of special steels used in electrical apparatus. Ware made from cast-iron containing 12 to 20 per cent silicon (tantiron, ironac) is acid resisting, and is hence employed in sulphuric acid works. Unfortunately it is very brittle.

Alloys of iron and nickel were first manufactured on an industrial scale in 1885, and since that time iron-nickel alloys have occupied an important place in industry. Both nickel and chromium increase the strength and hardness of steel, and consequently alloys of these metals and steel find employment in the manufacture of cables, armour plate, propeller shafts, engine forgings, aeroplane and car parts (crank shafts and axle gears). The automobile industry owes its existence to the special alloy steels. An armour-piercing shell of nickel steel retains its shape after passing through twelve inches of armour plate. Invar, an alloy patented in 1896, contains 36 per cent of nickel, and owing to its negligible change in volume with change of temperature it is used in the manufacture of measuring instruments, instruments of precision, and the pendulums of clocks. Elinvar, a similar alloy, is used for the balance springs of watches because its elasticity does not vary with temperature. A nickel steel alloy containing ·46 per cent of nickel, known as platinite, expands with rise of temperature at the same rate as glass does. It is therefore used for the lead-in wires of electric light globes and radio-valves. Nickeloy, which contains approximately equal amounts of nickel and iron, is used for making radio-transformer coils. Wireless has created a demand for a large number of new alloys with special electrical and magnetic properties.

Steel containing large proportions of nickel resists corrosion; hence the exhaust valves of engines are made from such steel. The addition of chromium to steel increases hardness and also the resistance of the metal to corrosion, and chromium-nickel steels containing 12 per cent of chromium find a use in the manufacture of rustless and stainless steel goods. A special acid-resisting alloy used in chemical works contains iron, nickel, chromium and silicon. Owing to its hardness, chrome steel is employed in the manufacture of projectiles, cutting tools, battleship equipment, and of machine parts subjected to much friction. Ferro-chrome alloys can be directly produced by smelting *chromite* (an ore containing both chromium and iron) with coke in an electric furnace. The introduction of a little vanadium—a comparatively rare metal that has recently found several uses in industry—to a steel containing 1 per cent chromium produces a tough, elastic and ductile alloy that resists fatigue under severe strains. Such steels are used for car and locomotive frames, for front axles, and for high speed tools. High speed tools are also manufactured from steels containing chromium, tungsten, and molybdenum: these steels remain hard even when red hot. Tungsten steel, or quick boring steel, contains about 3 per cent of chromium and a little vanadium. This steel, which is employed in making drilling and boring machines, has revolutionised workshop practice. Steel containing over 3 per cent of molybdenum is similar to tungsten steel, although less brittle; it is more expensive. The addition of vanadium to steel increases its strength, toughness, and elasticity, especially in conjunction with chromium. Cobalt, titanium and zirconium have also been employed in the manufacture of special steels. Cobalt steels retain permanent magnetism to an exceptional degree and are consequently used for permanent magnets for telephony and other purposes. Titanium—a metal shunned by the iron and steel manufacturers of a former generation because they thought that it made iron brittle—acts as a purifier by removing dissolved gases from iron and steel; vanadium acts in a similar manner, although it is employed primarily to alter the physical properties of steel. Titanium steels also possess strength and elasticity. During the war zirconium and nickel were added to steel to make it bullet-proof.

In the high speed steels now used some 20 to 30 per cent of the iron is replaced by other metals. Some of the new high speed alloys contain no iron at all. Stellite, which keeps a hard edge and actually gets tougher with rise of temperature, contains chromium, cobalt and tungsten. Although an effective substitute for platinum in jewellery, it is not employed as such on account of its cheapness. Cooperite, an alloy of nickel and zirconium, is lighter and cheaper than stellite.

Most of the alloying metals used in making special steels are added to molten steel in the form of ferro-alloys, that is, alloyed with iron. In most cases these ferro-alloys are produced in the electric furnace by the simultaneous reduction with coke of ores of iron and the metal concerned. Ferro-silicon is made by fusing the mineral quartzite (largely silicon dioxide) with iron scrap and coke in the electric furnace; ferro-chromium is produced by the reduction of chrome iron ore or chromite. Other important alloys are ferro-manganese, which is added to all steels, ferro-vanadium and ferro-tungsten.

If iron is the most useful of the metals then copper certainly ranks next to it in importance. Since this metal occurs in the native or metallic state, and since its ores are easily reduced it was one of the first metals to be used by man, who soon found that the addition of tin increased its strength and hardness. The alloy of tin and copper, bronze, being easier to melt gives better castings and does not retain blow-holes like copper. The name copper is derived from *æs cyprium*, the Latin for bronze, later shortened to *cuprium* (whence the symbol for copper, Cu); in Roman times copper ores were obtained from Cyprus. Although copper occurs native, especially near Lake Superior, the principal sources of the metal are the oxide and carbonate, which are present in the ores *cuprite* and *malachite.* Copper also occurs in the colouring matter of the feathers of some brightly coloured birds and in the blood of the cuttlefish, in which it is present as a compound termed haemocyanin. Like the haemoglobin of human blood, haemocyanin carries oxygen to the various tissues.

Copper is obtained from its ores by roasting and smelting with some form of carbon such as coal or coke, which reduces the oxide formed during roasting to the metal. In this process the carbon of the coal is oxidised to carbon monoxide by the oxygen of the ore, and the metal remains. Over a million tons of copper are produced in America every year, and this represents about two-thirds of the world's annual production. The oil process of concentration is extensively used to remove most of the impurities from the ore before smelting. The mixture of ore and *gangue*, or earthy material, is first crushed and agitated with water containing a little acid or alkali, and a little pine oil or tar oil added—about one pound of oil per ton of ore. A blast of air is forced through the liquid mixture and a froth of very small bubbles is formed. The ore particles, which are preferentially wetted by the oil, rise to the surface, while the gangue particles, preferentially wetted by the water, sink to the bottom. The froth is then mechanically separated and the ore smelted. In America the ore is roasted, fused with limestone, in a reverberatory furnace, and the *matte* or *coarse metal* run into a Bessemer converter through which a blast of air is passed. Impurities are thus oxidised, and if not gaseous at the temperature of molten copper, they form a slag. As the copper cools the dissolved gases present in the molten metal are expelled and the cold metal is consequently covered with small blisters. This is blister copper. It is further refined either by electrolysis (p. 108), or by melting and stirring the molten liquid with poles of green wood. The anode mud deposited in the electrolytic purification of copper contains gold and silver as well as other valuable metals. Eighty per cent of the world's copper is refined electrolytically. The process is carried out in long oblong tanks, containing anodes of partially refined copper and cathodes of pure copper. A solution of copper sulphate containing sulphuric acid serves as the electrolyte. The electrolysis takes from seven to fourteen days.

The bulk of the copper produced is used in the electrical industries. It is also employed in the manufacture of copper vessels and in the production of many useful alloys. Brass, an alloy of copper and zinc, is valuable for castings, and is used in place of copper for castings, cartridge cases, wire and ornaments. The golden lustre of the latter is increased by dipping in nitric acid and then polishing. Brass and some other alloys that have undergone severe mechanical stress are likely to develop "season cracking", especially if exposed to corrosive fumes or subjected to changes of temperature. The chance of cracking may be minimised by heating the alloy to a temperature of 200° C. to 300° C., the heat being sufficient to relieve internal stresses During the war special attention was paid to two varieties of brass, one a 70:30 alloy, used for cartridge cases, and the other a 60:40 alloy, the principal material for shell fuse-bodies. When nickel (10 to 25 per cent) is added to brass the alloy formed is white and hard. This alloy, German silver or white metal, originated in China under the name of *pakfong*. It is used as a substitute for silver in silver ware. An amalgam or alloy of copper and mercury becomes plastic at the temperature of boiling water, and after cooling sets hard within ten to twelve hours, a property that makes it suitable for dental stoppings.

Bronzes are alloys of copper and tin, although they may contain other metals. Aluminium bronze, a hard ductile alloy containing 5 to 10 per cent of aluminium, has a beautiful golden yellow colour that recommends it for household and ornamental objects. The new French bronze coinage contains 8 per cent of aluminium; English bronze coinage contains 95 per cent of copper, 4 per cent of tin, and 1 per cent of zinc. The addition of silicon to bronze increases its tensile strength. Phosphor bronze, containing about 10 per cent phosphorus is used for machine parts liable to receive much friction and for metal parts exposed to sea water or corrosive fumes. Gun metal is a bronze with from 8 to 12 per cent of zinc in it, and bell metal is a bronze containing from 12 to 24 per cent of tin.

Many other copper alloys of great industrial importance have been recently introduced. The addition of nickel to copper produces alloys that are much stronger than copper and possess the useful property of not being easily corroded. Cupro-nickel was employed during the war for bullet-sheathing. An alloy with 20 per cent nickel forms one of the most ductile of commercial alloys. It is used in automobile fittings, and takes a high polish. Constantan (58 per cent copper, 40 of nickel and 1 of manganese), the electrical resistance of which hardly changes with temperature, finds important uses in the electrical industry. Owing to the fine polish it takes constantan is used in the manufacture of table ware. Silveroid, an alloy of similar composition, is, as its name implies, a substitute for silver in table ware. Manganin (12 per cent manganese and 4 per cent nickel), and nickelin (25 per cent nickel and 20 per cent zinc) are two other copper alloys used in the electrical industries. Monel metal, an alloy of nickel, copper and iron, is rust and acid proof, and can be forged, rolled and welded. It is obtained directly from the nickel ore found at Sudbury, in Ontario. The alloy is employed for turbine blades, for machine parts that must resist corrosion, and for culinary articles.

Chemically speaking, gold and silver show a certain resemblance to copper, and they are nearly always present in small quantities in copper ores. Gold, which was probably the first metal known to man, occurs native in quartz veins and in alluvial deposits, the size varying from minute grains to large nuggets. Sea water contains small amounts of the precious metal, and many companies have been floated to extract it from the ocean on a commercial scale. Although ten thousand tons of sea water contain one gram of gold, the cost of extracting this is far greater than the value of the metal. The only gold obtained by companies floated for extracting the metal from sea water comes out of the pockets of foolish investors. Most of the world's gold is obtained from gold-bearing rocks, which are crushed and ground and then passed with water over cloth-covered plates. The gold adhering to the plates is treated with mercury, which dissolves it, and the gold-mercury alloy or amalgam distilled. Mercury distils off and leaves the precious metal. The residual gold-bearing sand is treated with a solution of potassium cyanide, which dissolves out the gold that escaped removal in the previous process. Gold is obtained from the cyanide liquors by the addition of zinc, which goes into solution and precipitates or throws down the gold. It is refined by electrolysis. For coinage or ornamental purposes gold is alloyed with copper or silver, or both. The purity or fineness of the metal is measured in carats, pure gold being taken as 24-carats. British currency gold used to have a fineness of 22-carats; the best jewellery is of 18-carat gold. Gold also finds employment in the preparation of ruby glass and porcelain, and in the form of gold chloride it is used for the toning of photographic prints. Gold plating is done in the same way as silver plating, that is by electro-deposition of the metal from a solution of gold cyanide in potassium cyanide, suitable amounts of silver and copper compounds being present. An alloy containing gold, silver and copper is thus deposited on the object.

Silver is generally found associated with lead and copper ores, and most of the silver used to-day is prepared as a by-product in the extraction of copper and lead. Some of the silver is also extracted by the cyanide process as described under gold. Silver is extensively used when alloyed with copper for coinage and for silver-plating cheaper metals. The so-called oxidised silver ware is not pure silver, neither is it oxidised. It is produced by depositing a thin film of silver on copper or brass, and then treating this with a solution of ammonium sulphide, which forms a film of black silver sulphide on the surface of the silver. As every housewife knows, silver readily tarnishes in air, especially in the air of large towns, and special silver alloys have been made in which copper, the usual alloying metal for silver, has been replaced by other metals conferring non-tarnishing properties on the silver. An alloy of 92·5 per cent silver with antimony is used under the name of "stainless silver" for table ware and toilet articles. Electro-plated silver articles are made by the electro-deposition of silver on copper or on copper-coated iron, the electrolytic bath consisting of a solution of potassium silver cyanide. The object to be plated forms the the cathode and plates of pure silver form the anode. Before the introduction of electrolysis on a commercial scale Sheffield plate was made by welding silver on to copper bars and rolling the compound bar into sheets. Silver salts are extensively employed in photography on account of the fact that they are acted upon by light. Photographic plates and films are covered with an emulsion of gelatin and silver bromide—a compound of silver and the element bromine.

Gold and silver have long been known as the *noble metals* because they are not acted upon by pure air; most other metals gradually oxidise and lose their metallic appearance. The platinum group of metals—platinum, iridium, osmium, palladium, rhodium and ruthenium—resemble gold and silver in this respect. Platinum has probably been known in an impure state from early times, but owing to its high melting point (1,755° C.) it was impossible to work it. The metal first became known in Mexico in the sixteenth century, and was called *platina del pinto* by the Spaniards; platina is a diminutive form of *plata*, silver. At one time the metal was so cheap that ingots of it were gilded and sold as gold. To-day, however, it would be more profitable to adulterate platinum with gold. Up to the time of the Russian Revolution the bulk of the world's platinum came from the Urals, but now the principal sources are Colombia, Ontario and the Transvaal. During the war when platinum was in demand for scientific work and the Russian supply fell off, alloys of the other members of the platinum family were used as substitutes. An alloy of 20 per cent palladium and 80 per cent gold—"palau"—proved quite effective for most chemical and dental purposes; "rhotanium" was another similar alloy. The alloy ilium is sometimes used in place of platinum. This consists of 60 per cent nickel, 31 of chromium, 2 of copper and tungsten and 1 of aluminium, silicon, manganese and iron.

Owing to its rareness platinum is much prized as a metal for jewellery. The addition of iridium increases the hardness of platinum and makes the metal less fusible. Iridium is a hard, white metal and when alloyed with other metals gives a hard-wearing alloy. It is used to a small extent in producing splendid black colours on the best china and porcelain. Platinum and alloys of platinum are employed in making scientific and surgical instruments. Its high melting point and resistance to the action of air and acids enables platinum to be used in the manufacture of dishes, crucibles, stills and other chemical apparatus that could not be made from ordinary metals. Platinum resistance thermometers are used for measuring high temperatures. The metal finds further use in the electrical industries for the manufacture of make and brake contacts in magnetos and induction coils, and in photography for platinotype prints—these possess great beauty owing to the variety of tones that can be produced. Platinum expands and contracts with change of temperature at the same rate as glass, and consequently platinum can be fused into glass without the latter cracking on cooling. On this account the metal was once used to make a connection between the filament of electric light bulbs and the fittings outside. It has now been replaced by the cheaper nickel-iron alloy, platinite, which is coated with copper so that glass will adhere to it. Osmium was once used as a metal filament in light bulbs, a use perpetuated in the name Osram, which still remains the trade mark of the General Electric Company. Osmium filaments have been exclusively replaced by tungsten filaments. Platinum has been used to a considerable extent in industry as a catalyst, or chemical activator (p. 198). It speeds up the rate of certain chemical reactions that are normally sluggish. In some respects its action might be compared with that of oil on machinery.

The metal tungsten has now become of first class importance in the electrical and radio industries, as well as in the manufacture of special steels. The metal is associated with iron and manganese in the mineral *wolfram* (whence the symbol W), from which it can be extracted by fusion with soda and subsequent treatment with acid. After strongly heating the residue, oxide of tungsten remains, and this is converted into the metal either by heating in a stream of hydrogen or with powdered aluminium. Ferro-tungsten, an alloy of iron and tungsten employed for manufacturing the intensely hard steels for high-speed machine tools, is produced by smelting wolfram with coke in the electric furnace. Other tungsten ores can be used, but iron ore or scrap iron must be added if the iron content of the original tungsten ore is not high enough.

The first electric lamp filament was of carbon. It was successively replaced by the metals osmium, tantalum, and finally tungsten. The early tungsten filaments were made by squirting the powdered metal mixed with a paste through dies. This method has been superseded by the use of drawn wire; the metal can in fact be drawn into wires of ·007 millimetre diameter. In the manufacture of tungsten wire the powdered oxide is compressed and heated first in hydrogen to 1,200° C. and then in an electric furnace to 3,000° C. The ingots obtained are then mechanically hammered into thin rods at the rate of ten thousand blows per minute, and the rods finally drawn through dies to form wire. Tungsten wire is also used in radio-valves. The filament in most dull emitting valves is made from tungsten containing 1 per cent of thorium oxide. In other types the wire consists of a core of pure tungsten or nickel, the emitting surface being coated with barium oxide or strontium oxide.

Owing to its high melting point (3,380° C.) tungsten is employed in the manufacture of refractory crucibles, X-ray targets and electrical contacts. It has a hardening effect on other metals, and enters into the composition of many important industrial alloys. Tungsten steels are used in drilling and boring machines, for permanent magnets in electric meters and magnetos, and for radio and telephone equipment. If tungsten were more plentiful and the metal easier to work it would eventually replace steel for purposes where strength, hardness and durability are needed. It is harder and stronger than steel, and is not subject to corrosion. Alloys of tungsten, carbon and cobalt are employed under the names of carboloy and widia (from the German, *wie Diamant,* like diamond) for making metal-cutting tools. As the name widia implies these alloys possess a diamond-like hardness. Before the war the tungsten trade was in the hands of Germany, although most of the ore came from Burma. The Admiralty actually bought the tungsten needed for armour plate and guns from Germany, and when the war broke out we were at first unable to work up the tungsten ore into the metal as the details of the processes were in the hands of German manufacturers. Sodium tungstate solution is used for fire-proofing fabrics. Fabrics soaked in the solution and dried will not burn with a flame, they will only smoulder.

Tungsten has a rival in the metal molybdenum, which is also employed in making electric lamps, radio-valves and high-speed cutting tools. Molybdenum is found usually as a sulphide, MoS_2, known as *molybdenite,* and as *wulfenite,* an ore containing lead and molybdenum. Ferro-molybdenum, the alloy of the metal with iron, is an electric furnace product made by fusing molybdenite with coke and lime. Molybdenum has been employed as a lamp filament support, and in the construction of X-ray and radio apparatus. The addition of a small amount of molybdenum to steel intensifies the characteristic action of any other metal present. It increases the tensile strength and toughness of steels, and during the war German howitzers were lined with molybdenum steel. Molybdenum-chromium steels have been successfully employed for the construction of aeroplane fuselage, propeller shafts, automobile parts and wherever great strength is needed.

The metals vanadium, titanium, zirconium, thorium and cerium are now extensively utilised in several industries, although not long ago the interest taken in them was purely an academic one. Vanadium was too rare to use on the industrial scale until 1903. In that year a rich deposit of vanadium ore was discovered in Peru, and since then the metal has found employment in the manufacture of steels and as a catalyst. Ferro-vanadium, the alloy added to steel, is produced by smelting vanadium ores in the electric furnace with iron and either silicon, ferro-silicon or coke. Vanadium can be prepared by heating vanadium oxide with aluminium powder, which combines with the oxygen and sets free vanadium. Vanadium increases the strength, toughness and elastic limit of steel, and vanadium steels have been employed in the manufacture of springs, connecting rods, axles and machine parts. Locomotive frames of cast steel contain 2 per cent of the metal. Vanadium oxide is used as a catalyst in the preparation of certain dyes, and some of its organic compounds are employed as "driers" for paints and varnishes.

Tantalum is chemically allied to vanadium—they are both members of the nitrogen group of elements—and it was formerly used a as filament in electric light bulbs. This marked its first industrial application. It has a high melting point, is malleable and ductile, and can be drawn into thin wires. Because of its resistance to corrosion tantalum has been used as a substitute for platinum in chemical apparatus, and it is claimed that the metal makes a definite improvement on steel for surgical instruments and special rustless steels. It allows an electric current to flow in one direction only, and as "Balkite" it enters into the construction of many rectifying units for converting alternating current into direct current.

Titanium is widely distributed on the earth, but the isolation of the metal on a commercial scale presents some difficulty. Its principal ores are *ilmenite* and *rutile*, from which the metal may be extracted either by the electric furnace method or by heating with aluminium powder. Until recently it had no technical applications. Indeed, it was originally avoided by the iron manufacturers who thought that it had a harmful effect on iron. Actually a trace of titanium in the form of ilmenite yields pig iron of good quality. It purifies steel and iron by removing dissolved gases from the molten metals; it thus removes blow holes and produces a denser and tougher metal. Titanium steels are used in the manufacture of steel rails, car wheels and crushing machines. The titanium is introduced into the steels in the form of ferro-titanium (10–15 per cent) or silico-titanium. Titanium oxide, a by-product of the gas mantle industry, enters into the composition of some abrasives and such refractory materials as crucible and furnace linings. The oxide is further employed in making artificial sapphires, in tinting artificial teeth and tiles, and as a white pigment (titanium white) when mixed with zinc oxide or white lead. Titanium white is used as a white "filler" for rubber, plastics and celluloid. Soluble compounds of titanium are employed in dyeing and in the preparation of cosmetics and printing inks. Titanium chloride gives off thick white fumes in air, and for this reason smoke screens were produced by means of it during the war. It is still used in aeroplane sky writing.

Zirconium, a metal used in the early metal electric lamp filaments, is a constituent of special steels. When added to steels and metal alloys it secures sound castings and increases the strength and resistance to acids. Zirconia, or zirconium oxide, has been used in the manufacture of special glasses and enamels, abrasives, glass cutters and refractory materials. Owing to the fact that it resists very high temperatures, fire-resisting crucibles, furnace linings and supports are made from it. A mixture of 90 per cent zirconium and 10 per cent magnesia makes an excellent resistive and high melting refractory lining for electric furnaces.

Cerium and thorium are used almost exclusively in the gas mantle industry. They are extracted from a mineral called monazite, which occurs in Brazil, India and Carolina. Besides these metals, monazite contains a large number of "rare earth" metals, including lanthanum, neodymium, praseodymium and samarium, and since practically no technical uses have been found for these they remain a drug on the market. Mesothorium, a by-product of the mantle industry, is used for coating objects to render them luminous in the dark. The thorium content of monazite is low and the cerium content high, and since the skeleton of the gas mantle consists of 99 per cent thorium oxide and only 1 per cent cerium oxide, large quantities of cerium are left over. When alloyed with iron cerium forms a "pyrophoric" alloy that emits sparks when struck with hardened steel, and for this reason a cerium steel alloy is used as the so-called flint in automatic cigarette and gas lighters.

Aluminium has assumed considerable importance during the present century; in fact it might well be called the wonder metal. Forty years ago only three tons a year were being produced; now over 110,000 tons a year are produced in Europe alone, the American output being only slightly lower than this. The rapid development and exploitation of aluminium has provided us with one of the romances of modern chemical industry. Most of the metal manufactured in this country is produced by the British Aluminium Company, whose output runs into a thousand tons a week. The factory of the company is supplied with hydro-electric power from Kinlochleven, a quiet spot that attracted the world-wide attention of engineers two years ago, when the Ben Nevis tunnel was opened. (*Plate* 17.) This tunnel is 15 miles long and 15 feet across, and is probably the largest of its kind. It is hoped that the cost of the project will be more than repaid by the cheap power now available, without which aluminium cannot be profitably produced. Its preparation by the electrolysis of a mixture of fused bauxite and cryolite has already been mentioned (p. 104). The process is carried out in rectangular shaped furnaces, from which the molten metal is withdrawn every few days. The silent working of the furnaces is one of the most impressive things that a visitor to an aluminium works notices. As the molten metal is withdrawn it is cast into various forms, which depend upon its future use. It may be cast into "notch" bars which are remelted for castings; it may be converted into "rolling slabs" weighing 400 lbs. for making sheet aluminium; or it may be drawn into "wire bars", about 3½ inches square, for preparing aluminium wire.

Aluminium is fairly soft, ductile and malleable, but not very strong, and for this reason the alloys are more valuable than the metal itself where strength is required. Being very light, aluminium is used in domestic utensils, but these must not be washed with strong soda or alkaline liquids since they attack it. In 1910, a new alloy, duralumin, was introduced, having excellent mechanical properties due to the addition of copper and magnesium to the aluminium. It can be tempered like steel and is fairly strong. Aeroplane castings are made from the super-light aluminium-magnesium alloys. Magnalium contains from 2 to 10 per cent of magnesium and is lighter than aluminium. During the last few years alloys of magnesium and aluminium have been introduced into the engineering industry, especially for automobile work and for the moving parts for such light machines as typewriters. An alloy of aluminium and zinc, with small amounts of magnesium, copper, silicon and iron was used by the Germans during the war for the framework of Zeppelins. Another German production, lantal, which contains aluminium alloyed with copper (4 per cent) and silicon (2 per cent) possesses the properties of duralumin. The English alloy L.8, which contains 11 to 13 per cent copper, is used for the pistons of internal combustion engines. The new alloys of aluminium with silicon and zinc have valuable properties; they can be cast so as to render subsequent machining and trimming unnecessary. In America small amounts of manganese (1 to 1·5 per cent) are added to aluminium for cooking utensils and for light forgings. Cutlery is now being made from an aluminium-copper alloy with the appearance of gold, and coloured aluminium ware that looks like enamel has just been introduced. These coloured goods are made by oxidising the aluminium article and dipping it into a suitable dye, which is precipitated on the layer of aluminium oxide on the surface of the metal. The new acid-resisting copper-aluminium-nickel alloy, Batterium metal, has proved to be very useful in constructing chemical plant subjected to corrosive liquids. It has exceptional tensile strength and ductibility, and can be easily welded or machined.

Owing to their lightness aluminium alloys have received many applications in the automobile industry and in aeroplane construction. Crank cases, radiator tops, petrol tanks, connecting rods, and the framework of aeroplanes are made from light aluminium alloys, chiefly those of the duralumin type. In 1918 the Allies employed 90,000 tons of aluminium for aeroplane construction. Sheet aluminium is now used as a panelling for cars, and the lightness of the metal makes its use possible in the metal parts of gramophones, metal furniture and military camping equipment. Powdered aluminium, made by stamping small pieces of thin sheet, forms the basis of some so-called silver paints; these are employed to cover the fabrics on aeroplanes and airships, as a paint to protect iron from rust, and as a protective coating for oil storage tanks to minimise the heating effect to the sun's rays.

In the electrical industry aluminium is a serious rival to copper, although its efficiency is only sixty per cent of the latter. If an alternating current supply be connected to two aluminium plates suspended in a solution of sodium bicarbonate, the current is rectified, that is the alternating current is converted into direct current. Aluminium thus acts as an electrolytic valve. It has been replaced by the thermionic valve and by so-called metal rectifiers, which consist of copper covered with a thin layer of copper oxide. Castings of aluminium are also suitable for use in electrical work as the metal is non-magnetic.

Aluminium foil is largely replacing tinfoil as a food wrapping and unlike tin it is not acted upon by foods. For this reason beer vats and fermenting vessels, previously made of copper, are now made of aluminium. Vessels of the metal are also employed for jam-making, fruit-preservation, and meat-extracting. The best varnishes are made in aluminium boilers.

Aluminium finds many applications in the chemical industries. Since it is not attacked by nitric acid fumes the metal finds employment in the nitrate plants of explosives factories, and because it does not rust, aluminium is used as a coating for iron, copper, and brass to prevent the atmospheric corrosion of these metals. In the "calorising" of iron the metal is baked with aluminium dust and a protective plating of pure aluminium is thereby deposited on the surface of the iron. A mixture of iron oxide and aluminium powder is known as thermit, and when the mixture is heated in a crucible by means of a magnesium fuse and barium peroxide a rapid chemical reaction occurs. The aluminium combines with the oxygen of the iron oxide, thereby liberating the iron, and the heat of the reaction causes the temperature to rise to 3,300° C. (6,000° F.) within half a minute. The molten iron formed may be tapped from the bottom of the crucible and allowed to flow on to two steel rails that are to be welded together. Or thermit mixture can be set up above broken machinery without dismantling it, and the molten iron run on to the broken parts to repair them. Thermit can be employed for welding locomotive frames and rails, and for repairing the broken stern posts of ships. Welding by means of thermit has been replaced to some extent by torch welding and electric welding. Electric welding enables rivetless steel ships to be constructed. The thermit process is similar to the blast furnace for iron smelting, only aluminium is employed instead of carbon to abstract the oxygen from the oxide in the ore. In the thermit process a carbon-free metal is produced and for certain purposes this is an advantage. Many of the rarer metals are now prepared by heating the oxide of the metal with aluminium powder. Tungsten, manganese, titanium, cerium, chromium, vanadium, molybdenum and their alloys with iron and copper are produced in this way. During the war thermit was used in incendiary bombs, and aluminium powder enters into the composition of ammonal, one of the modern explosives. Bauxite cement, or *ciment fondu*, is made by fusing lime and bauxite—the crude ore from which aluminium is obtained—and then grinding the product to a fine powder. Unlike ordinary cement it resists the action of sea water.

The preparation of magnesium by the electrolysis of the mineral carnallite has been previously mentioned. When burnt, magnesium gives out a brilliant white light and on this account it has long been used for flash-light powders in photography. Apart from this its use was very restricted until the introduction of the aluminium-magnesium light alloys. Steel makers have used magnesium for "scavenging", because the addition of the metal to molten steel secures firm strong ingots free from air holes. The alloy elektron contains magnesium (95) and zinc (5), with traces of copper and aluminium. During the war magnesium was in demand for signalling and star shells. The magnesium flares used by aviators to show up the enemy lines at night consisted of a stick of magnesium attached to a parachute, the whole being enclosed with an explosive powder in an iron case. When this was released from a plane the friction of the air rotated a pin which set alight the magnesium and fired the powder. This blew off the case and released the parachute to which the magnesium was attached. The glaring light of over 300,000 candle power produced by the burning magnesium lasted for ten minutes, and illuminated the ground at night sufficiently for aerial photographs to be taken or for bombing operations to be carried out.

Beryllium, a metal allied to magnesium, finds a very limited application in the manufacture of light alloys. It is prepared by Stock and Goldschmidt's electrolytic method. Beryllium fluoride is dissolved in a molten mixture of sodium and barium fluorides contained in a graphite pot, with an iron cathode, the temperature being maintained at nearly 1,300° C. Beryllium is deposited on the iron cathode. Recent research done at the National Physical Laboratory, Teddington, has shown that if only pure beryllium oxide could be produced cheaply, the cost of manufacture of beryllium would be little more than that of aluminium. Beryllium would be a very useful metal, but its scarcity is a serious obstacle to its technical employment on a profitable scale. At present the mineral *beryl*, a silicate of aluminium and beryllium, is the principal source of the metal; it only contains 4 to 5 per cent of beryllium. Beryllium is lighter and harder than aluminium and resists corrosion to a greater extent. It possesses a dark steel-grey colour, takes a high polish, and is as hard as steel. The alloys of beryllium with copper, silver, iron and aluminium have been the subject of investigation, and although there is no great demand for them in industry at present, their lightness, high melting point and hardness make them suitable for use in automobiles and aeroplanes. Where lightness, strength and corrosion resistance are essential, as in aero-construction, beryllium and its alloys might replace aluminium with advantage. The comparative rareness and difficulty of extraction prevent any widespread use of the metal. An untarnishable silver-beryllium alloy has been recorded. Small amounts of beryllium compounds were once used to toughen incandescent mantles.

The metal nickel has been employed for a considerable period in coinage, and there is evidence that ancient Chinese alloys contained it. Extensive deposits of the metal occur in New Caledonia and in the Sudbury district of Ontario, which produces about 88 per cent of the world's output. This is estimated at 40,000 tons per annum. In Canada the ores are roasted in heaps and smelted in a blast furnace, the *matte* obtained then being mixed with coke and salt cake (the residue obtained by heating salt with sulphuric acid) and smelted in an open hearth furnace, or in a Bessemer converter lined with silica.

The metal is purified by a process due to an English industrial chemist, Ludwig Mond (1839–1909). In the Mond process the crude nickel is heated to 80° C. in the presence of carbon monoxide—the poisonous gas present in coal gas and in the exhaust fumes from petrol driven engines—and the nickel is carried away in the form of the easily vaporised nickel carbonyl, $Ni(CO)_4$. The carbon monoxide is obtained by passing steam over red hot coke; this yields a mixture of carbon monoxide and hydrogen. The nickel carbonyl is vaporised, being thereby separated from impurities in the crude nickel, and decomposed by heat into metallic nickel and carbon monoxide, which can be used again for the extraction of more metal.

Nickel is used for plating iron, steel and brass, although chromium appears to be replacing it in this capacity. The nickel is deposited electrolytically from a solution of a nickel salt, usually nickel ammonium sulphate. Pure nickel is employed in the construction of dairy utensils and apparatus, and since it is non-toxic, domestic cookery utensils can be made from it. The metal also enters into the composition of many important alloys. Monel metal, an alloy of nickel and copper with a small amount of iron, is rust-and acid-proof, and finds considerable application in marine engineering. Over seventy tons of the alloy were employed in the construction of the *Europa* and *Bremen*, the new German Atlantic liners. Monel metal is used in domestic and restaurant equipment, for plumbing purposes, boilers, steam piping, valves, turbine blades and propellers. The propellers of the aeroplane, *Southern Cross*, were tipped with monel metal. Owing to the fact that the alloy resists corrosion, the metal equipment of dyeing factories and many chemical works is made from it. Nimol, an anti-corrosion alloy, consists of 75 per cent cast iron, 4 per cent chromium, and the rest monel metal.

Nickel silver, which incidentally contains no silver but copper, nickel and zinc, forms the basis of the best silver plated ware, and the alloy itself is used for cheap table ware and ornaments. Silveroid, a copper-nickel alloy containing 45 per cent of nickel, is extremely resistant to atmospheric corrosion. It is employed for metal shop fronts and table ware. An alloy of nickel (29·4 per cent), copper (64 per cent) and zinc (5·6 per cent) is known as ambrac. Copper-nickel alloys have found considerable application in naval engineering. Condenser tubes and air, oil, and water coolers for ship engines are now made from them.

Nickel steels and nickel iron-alloys—especially those that resist corrosion—have proved of great value in the chemical, engineering and electrical industries. Striking evidence of their value in architecture has been recently afforded by their selection in strengthening the concrete structure of St. Paul's Cathedral, India House, and other buildings. Many of the new iron alloys containing nickel and chromium resist not only corrosion, but high temperatures without oxidising or scaling, and at the same time possess strength and good mechanical properties. Such alloys are employed in the manufacture of chemical retorts standing temperatures in the region of 1,200° C., and for baffle plates, bolts, chains and screws; they have taken the place of iron and steel for annealing and case-hardening boxes. In the synthesis of ammonia, vessels are required to resist enormously high pressures and temperatures for some months, and the nickel-chromium iron alloys have been found to be definitely superior to steel for this purpose. A heat-resisting alloy of this class known as cronite is used in glass rolling and handling equipment, for the resistances in electric furnaces and domestic heaters, and for the exhaust valves of engines. The automobile industry now uses considerable quantities of nickel steels. A 5 per cent nickel steel is employed for case-hardened gears, and nickel alloy steels containing chromium and molybdenum were used to a very great extent in the construction of Sir Malcolm Campbell's car, the *Blue Bird*, which achieved the record speed of 253·9 miles per hour in February, 1932. The air speed record of 1931, won by Lieutenant Staniforth, was accomplished in a machine fitted with a Rolls-Royce 56 engine, in which many parts, including crankshaft, propeller shaft, hub, and rocker shaft tube were made of nickel alloy steels. The vital parts of locomotives, turbine wheels and shafts, special tools and firearms are made from nickel steels. As the proportion of iron in the nickel-chromium-iron alloys increases they merge into the class of stainless steels. Stainless steel for household purposes contains 12 to 14 per cent chromium and a little nickel. It is now being used in England and Germany for shop fronts. Firth's staybrite steel, a nickel-chromium corrosion-resisting steel, was used in the reconstruction carried out in Savoy Court, Strand.

Special nickel-iron alloys containing a high percentage of nickel, e.g. 70–80 per cent, have many applications in the electrical and wireless industries owing to their high magnetic permeability. The magnetic properties of permalloy (79 per cent nickel, 21 per cent iron), have made possible great advances in trans-oceanic communication by wire, the speed of communication being considerably increased by loading the cables with this alloy. Mumetal and hypernik (50 : 50 per cent) have similar properties. Exhibits at the 1931 National Radio Exhibition included "Permacore" low frequency transformers, the secondary windings of which were made of alloys of the above type. They have a number of applications in the lighter branches of electrical engineering. Nickel and nickel-iron alloys are employed in making the filaments and anodes of some radio valves. An alloy termed konel, used for this purpose, contains chiefly nickel with smaller quantities of cobalt, titanium and iron.

Nickel enters into the composition of certain aluminium alloys employed in the automobile industry. "Y" alloy and "R.R." alloy, which are essentially aluminium-nickel alloys with small amounts of copper, magnesium, and iron, have high tensile strength at high temperatures, and are consequently used for making cylinder heads and pistons, connecting rods, propellers and crank cases.

We have referred to cobalt as a constituent of special steels. This metal, which is extracted chiefly from ores found in Ontario, has only a limited application in its alloys with iron. Permanent magnets for telephony and other purposes are made from steels containing cobalt and tungsten, and special high speed cutting tools are manufactured from the alloy stellite (p. 127). Another alloy, festel metal, composed of cobalt, iron and chromium, is used for cutlery, and cochrome, an alloy of similar composition, finds certain applications in the electrical industries. Compounds of cobalt are used for making blue glass and enamels, and for colouring china. The pigment smalt is prepared by fusing silica with an alkali and oxide of cobalt. Plating with cobalt and cobalt-nickel alloys, has been tried; although apparently quite successful it has not received much application in industry. Organic compounds of cobalt have been used as "driers" for paints and varnishes. Invisible inks are made from cobalt chloride.

Chromium is a white metal that occurs in *chromite* or chrome iron-stone—an ore consisting mainly of the oxides of iron and chromium—and also in the precious stones, emerald, jade, ruby and garnet. Chromite is a very refractory substance, and when made into bricks forms an excellent furnace lining. It is the main source of chromium and its compounds. Ferro-chrome alloys, containing from 60 to 70 per cent chromium, are produced by smelting chromite with coal in the electric furnace. Metallic chromium is made by the method due to Goldschmidt, that is by heating chromium oxide with powdered aluminium in a refractory crucible. Chrome steel and the chromium iron alloys are produced by the addition of the required amount of ferro-chrome to steel. Chromium now rivals—if it has not superseded—nickel as a plating metal. It forms a surface harder than the best steel and exhibits a high resistance to abrasion and corrosion. In the manufacture of the best chromium-plated goods the metal object is first coated with nickel by electrolysis, and a layer of chromium deposited upon the nickel. This is accomplished by making the nickel-coated object the cathode in an electrolytic bath of chromium sulphate solution containing some chromic acid; a rod of chromium forms the anode. A deposit of ·0002 inch forms a sufficiently protective layer.

No phase of electro-deposition has caused such great interest nor found such a wide application as that of chromium-plating. The resistance of chromium to corrosion, its hardness and high polish enable chromium-plated goods to be successfully employed for all types of domestic metal work, for automobile parts including bumper bars, radiators and lamps, and for the bearing surfaces of machinery. The hard deposit of chromium affords a lasting, frictionless bearing surface and hence many machine parts are plated with the metal. Chromium-plated moulds used for rubber goods are unattacked by vulcanising chemicals, and chromium-plated printing plates are said to last considerably longer than the un-plated ones. Chromium plate is readily recognised by its characteristic bluish lustre.

Alloys of chromium, nickel and iron are used for armour plate, and compounds of the metal find employment in the photographic and tanning industries, in the production of pigments (chrome yellow and lemon chrome) and water-resisting glues and cements, and as mordants in the dyeing industry.

If we have neglected the metals zinc, lead and tin it is not because they are unimportant, but because they are no doubt familiar to the reader. The electrolytic refining of zinc has been recently introduced. Since air has scarcely any action on the metal it is used for galvanising iron and steel; this is done by dipping clean sheets of iron into molten zinc. In the Schoop metallising process, a zinc wire is fed into an oxy-hydrogen air blast, and the molten metal projected as a spray of minute droplets on the object to be coated. Iron can also be protected by heating it with powdered zinc to 430° C. (800° F.), when the latter attacks the iron and forms an alloy on its surface. When zinc was first extracted from its ores it was found to be brittle and unworkable, but it was soon discovered that its brittleness disappears on heating slightly above the temperature of boiling water. It can then be hammered into sheets and drawn into wire. Zinc is used in the manufacture of brass and German silver, in the construction of Leclanché and dry cells, and in sheet form it is employed for roofing and gutterings. On account of its cheapness cast-ware is made from it. "Delta metal", which consists chiefly of copper and zinc with smaller amounts of iron, manganese and lead, takes a high polish and resists atmospheric and acid corrosion. It can be cast, drawn and forged. Oxide of zinc is used as a pigment (Chinese white) and rubber "filler", and a mixture of zinc sulphide and barium sulphate constitutes the pigment lithopone. Unlike white lead this mixture does not darken on exposure to town air. Zinc sulphide is also used to make screens for X-ray work. Zinc chloride solution is employed as a timber preservative—it prevents dry rot—and as the basis of some dental stoppings.

Cadmium, a metal present in most zinc ores and hence a by-product in the extraction of zinc, is used for making fusible alloys, many of which melt in warm water. Wood's fusible alloy contains tin, lead, cadmium and bismuth. These fusible alloys, which melt at a very low temperature, can be employed as safety plugs in steam boilers, for electrical fuses, and in fire alarms. These applications depend upon the ease with which the alloys melt. Cadmium is a white metal with a bluish tinge. It takes a high polish and this, coupled with its anti-corrosion properties has made it a recent "find" in the electro-plating industry. It has been used to some extent as a non-corrosive plating metal, although it has the disadvantage of being more costly than most of the others. The deposition of nickel on cadmium has been tried, the cadmium supplying a rust-proof undercoat while the nickel gives the required finish. A copper-cadmium alloy finds employment in the manufacture of telephone and tramway cables, and an alloy of cadmium and mercury is used for filling teeth. The metal also appears to improve the casting properties of aluminium and decreases the staining properties of silver. Cadmium sulphide (cadmium yellow) forms the basis of certain yellow paints. When treated with selenium—an element resembling sulphur and obtained as a by-product in the electrolytic refining industries—it forms a pigment known as fine red or cadmium red.

Lead and tin were known to and widely employed by the ancients. The Phœnicians obtained their supplies of tin from Cornwall, where it was found as the oxide, *tinstone* or *cassiterite*, and for this reason Britain was known to the Mediterranean peoples as the Cassiterides or Tin Islands. The Cornish mines are no longer important; the bulk of the world's tin being produced in the Malay peninsula, Bolivia, Australia and South Africa. On account of its softness and malleability, tin can be beaten into thin leaves, and this property has led to its employment as a wrapping for food and cigarettes under the name of silver paper. Silver paper is really tin-foil. Large quantities of tin are used in making tin-plate; our so-called tin goods are not tin at all, they are only tin-plated. Tin-plate, used for making "tins", is made by dipping steel plates into molten tin, which forms a protective coating and prevents the steel from rusting. But once the tin surface is scratched and the iron beneath exposed to air and moisture it rusts far more rapidly than it would if the tin were not present. South Wales is the centre of the tin-plate industry.

When ordinary tin or white tin is cooled to a low temperature it crumbles to a grey friable powder known as grey tin.

At all temperatures below 18° C. this grey form of tin is likely to be formed, and since it appears on the white tin in the form of a powdery growth it is known as tin pest or tin plague. Organ pipes and tin roofs have been known to crumble and go to pieces when attacked by the tin plague, which is moreover contagious, since the conversion of white tin into grey is hastened by contact with the latter.

Tin enters into the composition of many useful alloys. Alloyed with lead it forms common solder and pewter. Britannia metal and Babbitt metal contain tin, copper and the metal antimony. When molten antimony solidifies it expands slightly, and hence molten mixtures of antimony and other metals when poured into moulds take very fine and sharp impressions. Antimony is thus a constituent of type metal and linotype metal, which also contain lead and tin. These alloys are used for the type in printing.

Lead is found usually as the sulphide in the mineral *galena*, from which it is obtained by roasting in a current of air. It is a bluish-grey metal, exhibiting a bright metallic lustre when freshly cut. This grows dull on exposure to ordinary air, but perfectly dry air and air-free water have no action on the metal. In moist air or in aerated water lead becomes covered with a film of lead oxide and finally lead carbonate. When soft water flows through lead water pipes it dissolves some of the metal and since lead compounds are distinctly poisonous, the continued use of drinking water containing lead would lead to lead-poisoning. This solvent action is checked by the carbonates and sulphates of magnesium and calcium which are normally present in hard water. They form a coherent lining of lead carbonate on the inside of the lead piping and thus prevent any more lead from being dissolved. When the water supply of a district is very soft the water is hardened by the addition of a little lime. Owing to the poisonous nature of lead it cannot be used in cooking utensils.

Lead is a very soft, heavy and easily fusible metal, and when heated can be squirted into wire or tubing. The metal itself is widely employed for roofing and plumbing purposes, as a lining for tanks and acid-chambers, and in the manufacture of lead accumulators. Frary metal, from which bearings are manufactured, is an alloy of lead containing small amounts of the metals barium and calcium. The compounds of lead, especially the oxides and carbonates, find extensive application in many industries. Red lead, formed by heating litharge or lead monoxide in air, was used as a pigment in classical times and during the Middle Ages. It is now used for making flint glass, pottery glaze, paints and matches. When red lead is treated with nitric acid a chocolate brown powder—lead dioxide or peroxide—remains. We have seen that this oxide forms one of the plates of the lead accumulator. White lead or basic lead carbonate, is largely employed as a pigment, and in the manufacture of pottery glazes. It mixes easily with linseed oil and confers on paint its covering power, but unfortunately it darkens on exposure to air, especially the air of towns. This is due to the fact that air contains traces of sulphuretted hydrogen, the gas that smells like bad eggs, and this acts upon the white lead, forming black lead sulphide. For this reason many white paints are made up with zinc oxide, lithopone (p. 146), or a mixture of titanium oxide and barium sulphate. These substances, however, have low covering power. White lead is manufactured by placing lead plates in earthenware pots containing a layer of acetic acid (the acid present in vinegar). The pots are stacked in rows on a bed of spent fermenting tanner's bark or dung, and then covered with boards. More pots are placed on top of these boards and eventually several tiers of pots are built up, each tier standing on boards covered with fermenting bark. This bark produces heat and gives off carbon dioxide, which converts the basic lead acetate, formed by the action of the acetic acid on lead, into basic lead carbonate or white lead. A modification of the above method for making white lead was described by Theophrastus (373–287 B.C.).

Our knowledge of the production and applications of metals has rapidly grown during the last fifty years. Before 1890 aluminium was not a commercial metal; now it is a necessity. The same can be said of many other metals. Five years ago chromium-plated goods were unknown to the public; to-day they are in demand everywhere. No other electro-deposited metal has found such a wide application as chromium. The special alloy steels have revolutionised engineering, and with the light metal alloys they have made possible high-speed cars and aeroplanes. Progress has been exceptionally rapid during the present century, and if it is maintained we shall witness the introduction of many new industrial alloys and the technical application of metals that are only chemical curiosities at present. No technical uses have been found for lithium, indium, niobium, scandium, germanium, gallium and a host of the rarer metals, although they have been extensively studied by chemists. But the history of applied chemistry has shown that facts of apparently merely academic interest can often be adapted to the needs of modern civilisation. The pure science of to-day is the technology of to-morrow.

CHAPTER VII

FUELS AND ILLUMINANTS

At an early period in his civilisation man worshipped the sun as the source of all energy and life. The chemist knows that practically all the energy on the earth has originated from the sun, with the possible exception of that produced by the tides. At the present day most of the energy required by man for domestic and industrial purposes comes from the heat liberated during the combustion of the element carbon and its compounds. These have been stored up on the earth in the form of wood, peat and coal by the agency of the sun. The heat that we obtain by burning these and other fuels came originally from the heat of the sun, which has helped to elaborate the foods upon which our life depends. Green plants contain a green colouring matter known as chlorophyll, which has the power of trapping the radiant energy of sunlight and of using it to effect the combination of water vapour and carbon dioxide. Energy is needed to make water and carbon dioxide react with one another and this energy is obtained by plants from the red rays of sunlight. It is supposed that first of all oxygen and a substance called formaldehyde are formed in the cells of the green plant—

$$\underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water vapour}}{H_2O} = \underset{\text{formaldehyde}}{CH_2O} + \underset{\text{oxygen}}{O_2}$$

and that several molecules of the formaldehyde unite to form a sugar, similar in composition to glucose—

$$\underset{\text{formaldehyde}}{6CH_2O} = \underset{\text{a sugar}}{C_6H_{12}O_6}$$

From sugars the plant builds up *cellulose*, which is the main constituent of the framework of plants, and starch, one of their principal storage foods. Although the wonderful mechanism by which nature brings about these vital changes is quite unknown to us we are dependent upon it for our food and our fuel. The sugar and starch of plants are the source of our bodily energy; they enter into the composition of our foods. When they are slowly oxidised or burnt up within our body, carbon dioxide and water vapour are produced, and the change results in the setting free of energy which we require to maintain our vital activity. During the respiration of animals and human beings, the carbon-containing bodies in their living tissues are oxidised by atmospheric oxygen into carbon dioxide. This in turn is built up by plants into compounds such as sugar, cellulose and starch, which once again become available as foods or energy producers. Green plants are energy transformers; they transform the radiant energy of sunlight into the potential energy of combustible substances containing carbon.

With the exception of natural oils—the origin of which is still obscure—all fuels may be regarded as derived primarily from cellulose. This substance is an essential constituent of wood and peat, in which it has undergone a slight metamorphosis, and also of lignite or brown coal. All forms of coal, from bituminous to anthracite, have been formed from it by a slow process of carbonisation. Whether we burn these cellulose derivatives as we find them in nature, or whether we convert them first into charcoal, coke and gases, we are recovering the energy stored up from the sun. Heat is one form of energy which may be converted into other forms, e.g. mechanical, light and chemical energy. Similarly, the latter can be converted into heat and light energy. Chemical energy is stored up within the molecules of combustible substances, which on combustion combine with the oxygen of the air. Energy is liberated in the form of light and heat. The process of combustion may be compared to the running down of a clock; potential—or stored up—energy is released and becomes available for doing work. Combustion is a chemical process in which chemical energy is transformed into an equivalent amount of other forms, chiefly heat. When we burn coal we convert the potential chemical energy of its molecules into heat energy.

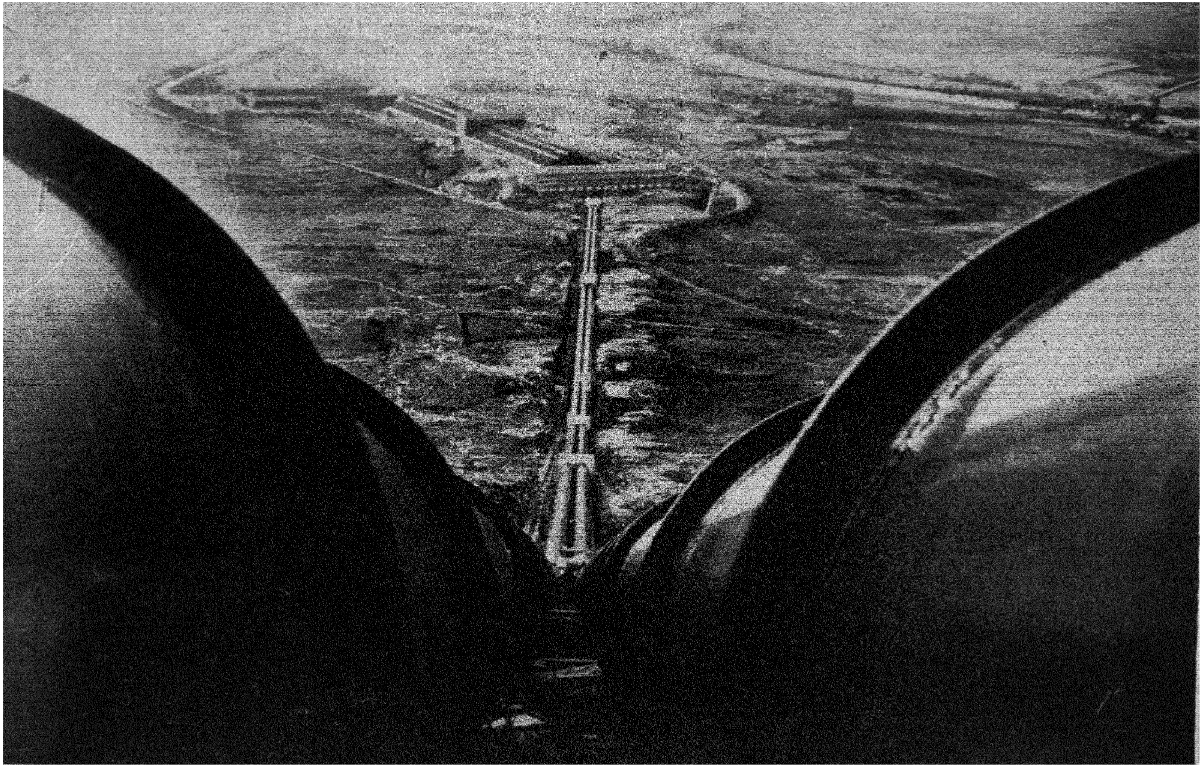
The first fuels and illuminants employed by man were vegetable and animal fats and wood. In these days of cheap artificial illumination we find it difficult to imagine the conditions of life when our ancestors used rushes and twigs dipped in olive oil and other vegetable oils as a source of light. Eventually lamps fitted with wicks of vegetable fibre were introduced for burning the oil, and later still the need for a vessel to hold the oil was dispensed with by using solid animal fats. The earliest candles were made by dipping rush wicks or dried plant stems into melted ox-fat or tallow. At a later date wicks of cotton fibre replaced rushes. It was once the custom for the industrious housewife to save the waste fats of the kitchen for candle making, but since the beginning of the last century, candle making has gradually passed into the hands of the manufacturer.

The development of the modern candle industry was made possible by Chevreul's discovery of the nature of fats and oils. Chevreul, who holds the record for longevity among chemists, died in 1889 at the age of 103. His researches on fats, carried out between 1811 and 1823, showed that these substances are compounds of glycerin and certain acids, which on account of their greasy nature are called fatty acids. The most important of these are palmitic, stearic and oleic acids. Solid fats contain mainly glycerin combined with palmitic and stearic acids, both of which are solid; liquid fats consist chiefly of a compound of glycerin and liquid oleic acid, an important constituent of olive oil. When the old-fashioned tallow candles were burnt, the liquid compound of oleic acid and glycerin ran down the side of the candle and caused it to gutter, and at the same time the glycerin gave rise to an acrid smelling substance termed acrolein. The modern candle contains no oleic acid and no glycerin—glycerin is too valuable to burn in candles. In the manufacture of modern candles the animal fat or tallow is boiled with acidified water to separate it from fibrous matter, and then heated with superheated steam and slaked lime, which break down the fat into glycerin and palmitic, stearic and oleic acids. After separating the glycerin, the mixture of acids is warmed and pressed to remove the liquid oleic acid, and the remaining solid, which consists mainly of stearic acid or stearin, is then incorporated with paraffin wax. Paraffin wax, which was once chiefly obtained by distilling Scottish shale (p. 175) in large retorts, is now made in Germany by distilling brown coal or lignite, and large quantities are also obtained from American, Galician, and Burmese petroleum. Unlike glycerin and the previously mentioned acids, which contain carbon, hydrogen and oxygen, paraffin wax consists of a mixture of substances containing carbon and hydrogen only. These are therefore known as *hydrocarbons.*

When a candle burns the wax melts and is drawn up the wick into the flame, where it is vaporised. The vapour of the various hydrocarbons present in the wax then burns, forming carbon dioxide and water vapour. In the old tallow candles the wick had to be snuffed or clipped to prevent the candle from guttering. This was because the unburnt vapour from the hot tallow surrounded the wick and prevented the oxygen of the air from reaching it. The wick thus became charred but did not burn away, and as it gradually increased in length more liquid tallow passed up it than could be properly vaporised and burnt. The candle then burnt with a low, sooty flame. In 1825 a solution to the candle snuffing problem was found; twisted or flat, plaited wicks were then introduced. When the candle burns, the end of the twisted wick curls or bends over to the outer part of the flame and slowly burns away, since it has access to the oxygen of the air.

The so-called wax candles of our forefathers were made from beeswax, which although much harder, is similar in composition to the ordinary fats and oils. It consists mainly of a compound of palmitic acid, one of the acids present in palm oil, and a white greasy substance termed melissyl alcohol. Spermaceti, a solid waxy-like substance obtained from the head of the sperm whale, is also employed in the manufacture of expensive candles. In China and Japan hard vegetable waxes are used.

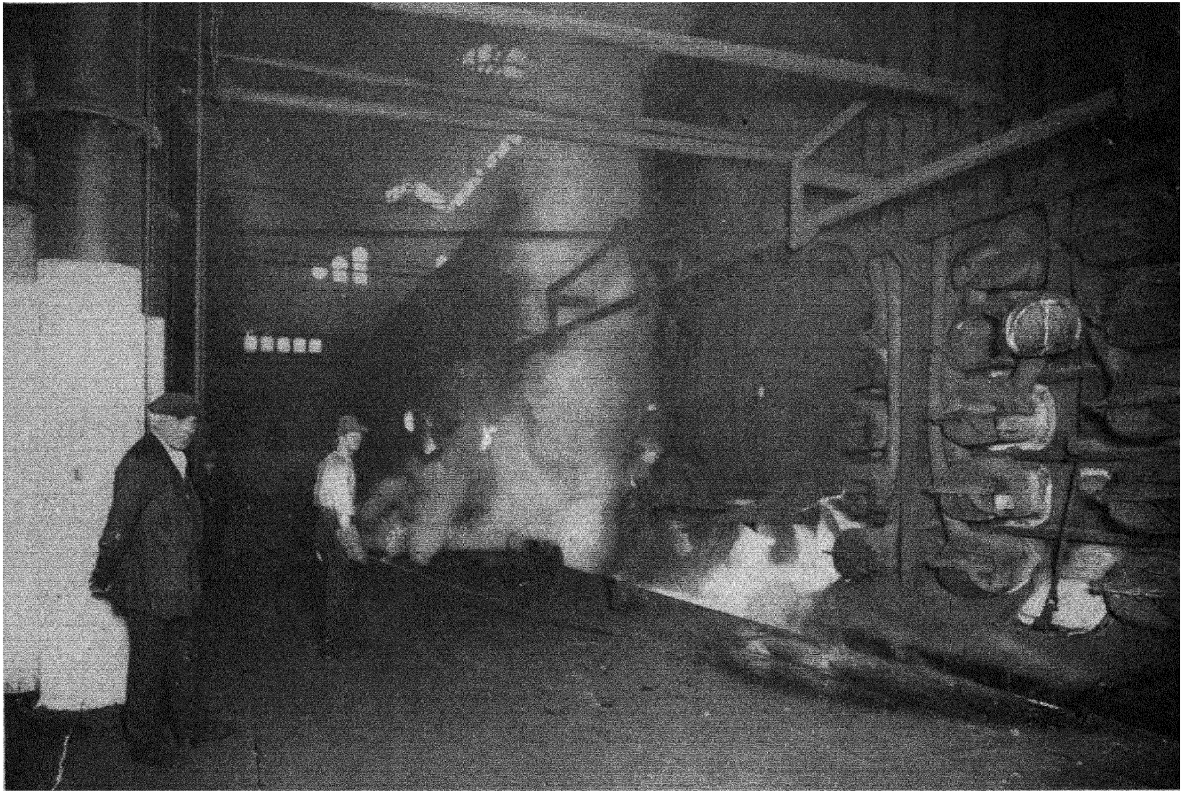
If the animal and vegetable fats supplied man with his first illuminant, wood was his first fuel. Although in industrial centres wood as a fuel has been superseded by coal, it is still used locally in well-wooded countries. For domestic purposes there is much to recommend a cheerful wood fire. From the economic point of view we must remember that wood contains much water—from 20 to 50 per cent based on the weight of dry fibre —and that compared to coal it has a low heat-producing power,



[*By courtesy of Messrs. The British Aluminium Co., Ltd.*

Plate 17.—GENERAL VIEW FROM THE PORTAL OF A PIPELINE OF THE POWER HOUSE AND ALUMINIUM FACTORY AT LOCHABER (See p. 137.)

[*Face page* 154



[*By courtesy of Gas Light and Coke Co., Ltd*

Plate 18.—Discharging Retorts at the Beckton Gas Works (See p. 160.)

or *calorific value.* The calorific value of a fuel is the number of heat units produced by the combustion of a unit weight of fuel. Wood consists largely of cellulose ($C_6H_{10}O_5$), which as the formula shows, contains the elements carbon, hydrogen and oxygen. The hydrogen and oxygen are in the ratio to form water, i.e. two atoms of hydrogen for every atom of oxygen, and we can consequently regard the hydrogen as being already oxidised or burnt. When cellulose is burnt the heat liberated, or the heat of combustion as it is called, is the same as that produced by the combustion of the carbon contained in it. Although oxygen and hydrogen constitute 56 per cent by weight of cellulose, they contribute nothing towards the heat produced when cellulose burns; the heat is derived from the combustion of the carbon. Wood, which contains slightly more carbon than cellulose, has a higher calorific value than the latter, especially if resinous, e.g. pine, fir and spruce wood. It has long been known that if wood be burnt slowly in a limited supply of air, it is converted into charcoal, and before coal came into use this substance was extensively employed as a fuel. The main constituent of charcoal is carbon, and hence a given weight of charcoal gives out more heat than the same weight of wood. (Charcoal is used in the manufacture of iron, steel and gunpowder, and owing to its porous nature it forms an excellent filtering medium. Its porous, foam-like structure enables it to condense or *adsorb* many gases;) for this reason sewers and foul places are purified or sweetened by means of charcoal. During the war gas masks were filled with charcoal made from coconut and nut shells, and charcoal biscuits have been used medicinally for absorbing gases in the alimentary tract in cases of indigestion. Commercially, charcoal is manufactured by heating wood in ovens or retorts from which air is excluded. In this way many valuable gaseous and liquid products are reclaimed. These escaped into the air and were lost in the older process of allowing wood to smoulder slowly in charcoal pits. The by-products obtained by carbonising wood in retorts include wood tar, wood spirit and combustible gases. Wood spirit contains acetone and methyl alcohol, both of which are widely used in the paint and varnish industry. Methyl alcohol is also used in the manufacture of dyes, drugs and photographic chemicals, and acetone finds a special application as a solvent, for example in the manufacture of cordite and collodion (p. 216).

When wood or vegetable matter rich in cellulose slowly decays in a moist soil or beneath water a series of chemical changes sets in. Minute organisms in the soil decompose the cellulose, eliminating its hydrogen as marsh gas or methane—a compound of hydrogen and carbon—and its oxygen as carbon dioxide. These changes are going on in stagnant ponds, as we can prove by stirring up the water with a stick. The bubbles of gas that rise to the surface have been shown by chemists to contain marsh gas and carbon dioxide, both of which have been formed by the slow decomposition of the cellulose of dead plants. As a result of the gradual elimination of hydrogen and oxygen the product remaining becomes increasingly rich in carbon, and if the process continues long enough, especially in the absence of air, the product possesses a composition similar to that of coal.

Coal, in fact, consists of the fossil remains of the prehistoric luxuriant forests that once covered the earth. By the gradual carbonisation of the woody fibre or cellulose of the plants, the materials peat, lignite, or brown coal, bituminous or household coal, and anthracite have been formed. These substances represent successive stages in the natural carbonisation of woody tissue below the earth's surface. Peat consists of vegetable matter that has undergone carbonisation and decomposition for a much shorter time than anthracite, and since it has not been subjected to such great pressures as the latter or as coal, it is consequently less compact.

An examination of the carbon hydrogen and oxygen content and the calorific value of various natural fuels is very instructive:

	Carbon	Hydrogen	Oxygen	Calorific Value
Wood.........	50	6	44	8,600 B.T.Us.
Peat.................	60	6	34	9,900 "
Lignite..............	67	5	28	11,700 "
Bituminous Coal...	88	6	6	15,000 "
Anthracite..........	94	3·5	2·5	15,750 "

As we pass from wood to anthracite through substances representing successive stages of carbonisation, the hydrogen and oxygen content falls off but the calorific value increases. We see that coal gives out more heat than wood; this is because coal contains more carbon per given weight than wood. When wood burns it gives a blazing, luminous flame on account of the large amounts of inflammable gas given off, and for this reason wood burns more readily than any other solid fuel. The inflammable gases formed when wood is heated consist mainly of hydrocarbons derived from the carbon and hydrogen of the wood. Anthracite and coal, which represent advanced stages in the carbonisation of wood, contain little hydrogen and hence give off only a small amount of inflammable hydrocarbons on burning. This accounts for the fact that anthracite is very difficult to ignite and burns without producing much smoke or flame; anthracite is 94 per cent carbon. It is unsuitable for domestic use unless burnt in special stoves, and on account of its high calorific value it forms a most important industrial fuel. From the table given it is seen that the calorific value of the natural solid fuels increases with progressive carbonisation, and this explains why anthracite is superior to all other solid fuels. The calorific value of a fuel is usually measured in terms of British thermal units, a unit being the amount of heat required to raise the temperature of one pound of water 1° Fahrenheit; a British thermal unit equals 252 calories. If we are going to obtain value for our money we should not buy coal according to weight alone but according to its heat-producing value. Thus it might be more economical to purchase a good coal at say 45*s*. per ton than a cheaper grade at 40*s*. In America and on the Continent coal is not sold by weight alone; an indication is given of its calorific value. Unfortunately the law and the public are so apathetic in this country that coal is still sold by weight and the consumer finds out by bitter experience which type of coal suits his purpose best.

When George Stephenson was asked what drove his locomotive he replied: "Bottled-up sunshine." Coal *is* bottled-up sunshine. Although the bottling-up is still going on in the manner we have indicated, and although coal is still being formed by the carbonisation of woody tissue, we are using up coal faster than it is being formed. Coal is our main source of fuel; in spite of the increasing use of oil as a fuel and the development of water power, coal still furnishes three-quarters of the world's energy supplies. In America, where much petroleum is consumed as a fuel, coal still accounts for 70 per cent of the energy supplies; petroleum and natural gas account for 25 per cent and water power for 5 per cent. Coal constitutes the capital of any nation and all the nations are living on their capital. It has been estimated that at the present rate of coal consumption in this country—some 300,000,000 tons per annum—existing coal fields will be exhausted in 500 years, and this means that civilisation as we know it will be endangered, if not destroyed. The economic utilisation of our coal supply thus becomes a matter of national importance. The rate at which our coal reserves are diminishing is about nine times that of the United States, which possesses half the world's available coal. We must not only regard coal as a fuel that supplies us with heat and energy; it is also the potential source of dyes, fertilisers, explosives, drugs, perfumes, antiseptics and most of our organic chemicals. It has been estimated by experts that the world's coal reserves will be depleted in less than a thousand years. The world's supplies of petroleum and natural gas appear to be running short as well. Although the actual production is on the increase, this is due, not to any increased output from the existing oil wells, but to the discovery of new ones. Oil wells rapidly run dry and we cannot assume that new ones will always be discovered to avert a fuel famine.

It might be suggested that we should use wood more than we do as a fuel. Although much wood is still burned locally in well-forested regions it would be sheer folly to denude our forests in order to use wood as an industrial fuel. We must remember that without green vegetation both animal and human life would cease to be; the green plant breaks up the carbon dioxide breathed out by human beings and animals, keeps the carbon, and returns the oxygen to the air. Green plants thus keep the air fresh and prevent the accumulation of carbon dioxide which in large quantities would cause asphyxiation. As it is, large quantities of timber are cut down in America and Europe for building purposes and for paper-making, without making good the loss.

Peat is used in countries lacking large coal supplies, e.g. Ireland, Russia and Denmark. In Ireland alone 7,000,000 tons of peat are consumed for fuel annually, and in Russia there are 100,000,000 acres of bogs capable of yielding 125,000,000,000 tons of peat. In its natural state peat contains from 80 to 95 per cent water, which must be driven off before the peat can be used as a fuel. This is usually effected by exposing the peat to air, or by subjecting it to high pressure. Much peat is also converted into briquettes for burning by what is known as wet carbonisation; the wet peat is compressed and heated to 200° C. and the product briquetted in a press. Owing to its bulky nature it is not economical to transport peat and for this reason the consumption of this fuel is mainly local. One and two-thirds of a ton of air-dried peat generates as much heat as a ton of coal. It is used principally for power purposes and for the production of combustible gases.

Lignite or brown coal, is intermediate in properties and calorific value between peat and coal and as a fuel it has found considerable use, especially on the Continent, where it is converted into briquettes by heating under pressure. Much coal dust and small coal is made up into briquettes for domestic consumption by moulding under pressure either with or without a binding material, such as pitch or tar. In Germany, where 150,000,000 tons of lignite are used per annum, this fuel is efficiently employed for steam raising, running power stations and for railway purposes. The inferior grades are also distilled to yield extremely valuable tar products and ammonia.

Whilst wood, coal, peat and lignite supply local needs, coal is the most important of our industrial fuels. Chemists have long realised that if we are to utilise coal in the most economical manner we must know something about its physical and chemical constitution. Coal is a highly complex substance formed by the decay of cellulose and another vegetable product termed lignin. Considerable information on the chemical nature of coal has been obtained by treating it with various solvents; by observing the action on it of certain chemical reagents, e.g. oxygen, hydrogen and chlorine; by submitting it to distillation at various temperatures; and by a careful microscopic examination. Dr. Marie Stopes has microscopically distinguished and isolated from coal four different constituents which she has termed *fusain, durain, clarain* and *vitrain.* Fusain, or mother of coal, the remains of the woody cell fibres of plants, consists of powdery fibrous strands. Durain, which is dull, hard and compact, has a granular structure. Clarain contains such plant remains as stem and leaf tissue, spores and cuticle; it is bright and glossy but always streaky in appearance. Vitrain, more brilliant than clarain, possesses a uniform texture and has the nature of a hardened glue or jelly. The bands of vitrain are entirely devoid of plant structure, and in this respect resemble *dopplerite,* which is found in peat. When fresh this is soft like india-rubber and can be broken with the thumb nail into flakes. These four constituents confer upon coal some of their characteristic properties. Thus the coking properties of certain coals appear to be due mainly to clarain, and coals leaving a large ash contain much fusain. By prolonged extraction with certain solvents it has been shown that the substance of coal can be divided into three compounds or groups of compounds, which have been distinguished by the letters, α, γ and β. The α- and β-compounds are supposed to be derived from the cellulose of the original plants and on distillation they give rise to gases mainly composed of hydrogen and oxides of carbon. It is assumed that the γ-compound is derived from the oils, resins and waxes of plants, and this on distillation yields gases rich in hydrocarbons and half its weight of liquid products. The major portion of the coal tar formed by the distillation of coal would appear to come from the γ-compound.

When coal is submitted to what is known as *destructive distillation* by being heated in iron retorts (Plate 18) in the absence of air, it forms a variety of products, the nature of which depends upon the kind of coal used and the temperature of distillation. Destructive distillation, unlike ordinary distillation, involves a chemical decomposition of the compounds present in the coal, the carbon, hydrogen and oxygen atoms being re-arranged to form new compounds, that are not found as such in the original coal. When *bituminous* coal or *cannel* coal—so-called because when heated in air it will burn like a candle—is distilled in retorts in the absence of air, the main products are coke, which is left in the retorts, coal-gas, coal tar and a watery liquid containing ammonia. The latter is derived from the nitrogen compounds in coal and is the source of some of the ammonium sulphate used as a fertiliser. Anthracite yields hardly any volatile products when subjected to destructive distillation because its hydrogen and nitrogen content is low; the gaseous and liquid products of coal distillation are mainly compounds containing carbon, hydrogen and nitrogen.

Gas-coke consists of about 95 per cent carbon, although its actual composition depends on the temperature of distillation or carbonisation. The coke obtained as a by-product in the manufacture of coal gas results from the so-called high temperature carbonisation of coal, in which the distillation is carried out at 1,000° C. Such coke has a calorific value of about 13,000 British thermal units, and although it is used industrially as a furnace fuel and as a source of gaseous fuels (p. 177), it is not suitable for domestic purposes since it is difficult to burn in grates. Coke finds extensive use in the metallurgical industries for obtaining metals (e.g. iron) from their ores, and large quantities required for this purpose are produced by heating coal in special coke ovens. The coke should be fairly dense and contain as little sulphur and ash as possible; these are objectionable impurities from the metallurgical point of view. Gas coke is not ideal for metallurgical work, and in this country alone 12 million tons of coal are annually converted into metallurgical coke. In the older coke ovens the valuable by-products—gas, coal tar, ammonia—were allowed to escape into the air, but most of the ovens now in use are fitted with appliances for recovering these by-products.

Coal-tar, which is useless as a fuel, contains a number of extremely useful substances. This dirty sticky substance, once regarded by the gas manufacturers as a necessary nuisance, is now the chemist's source of benzene, naphthalene (the main constituent of "moth balls"), creosote oils, carbolic acid and the cresols. Actually about two hundred different substances are present in coal tar. Since the most important constituents have different boiling points the coal tar is re-distilled and the distillates collected in various fractions. The *light oil* which distils over up to 170° C. contains the hydrocarbons benzene, toluene and xylene; these are used as solvents and serve as the source of aniline dyes, explosives and drugs. Benzene is also important as a fuel for motor engines. Between 170° C.

and 230° C. the carbolic acid oils distil, and these can be separated into naphthalene—which in addition to being used as a moth preventive is the starting point in the preparation of synthetic indigo—carbolic acid and the cresols. The latter are extensively used in the manufacture of disinfectants and antiseptics, e.g. Lysol, Jeyes' Fluid. Carbolic acid is the source of an important explosive named *picric acid*. Creosote oils, which distil over between 230° C. and 270° C., are employed for the preservation of timber. The last fraction obtained by distilling coal tar contains *anthracene*, an important product used in the preparation of many dyes.

Although Boyle and certain other seventeenth century chemists had noted that coal gives off an inflammable gas on distillation, some hundred and thirty years elapsed before coal gas was used generally as an illuminant. In 1793 William Murdock lighted his house at Redruth with coal gas, and six years later he employed it on a large scale at a factory in Birmingham. In 1810 Winzer founded the Gas Light and Coke Company, which supplied a large number of London consumers in the early part of last century. Considerable opposition resulted from the candle makers and oil sellers, but the population gradually realised that the new method of lighting was a vast improvement on the old. The gas obtained by distilling coal carries with it tarry matter and ammonia, which can be condensed by cooling the gas. It is then further purified by passage through chambers called "scrubbers"; these are filled with coke over which water trickles (Fig. 27). The gas still contains traces of that objectionable smelling gas, sulphuretted hydrogen, and this is removed by purifiers containing oxide of iron. When the purifiers get fouled the oxide of iron, which now contains about 50 per cent sulphur, is sold for the manufacture of sulphuric acid. Another impurity in coal gas that contributes towards the cost of production, is the highly poisonous compound of carbon hydrogen and nitrogen termed prussic or hydrocyanic acid. This is removed and converted into potassium ferrocyanide (yellow prussiate of potash), the parent substance of prussian blue and potassium cyanide. After purification the coal gas passes into gasometers or gas holders from which it is led into the gas mains for distribution to consumers. During recent years it has been the

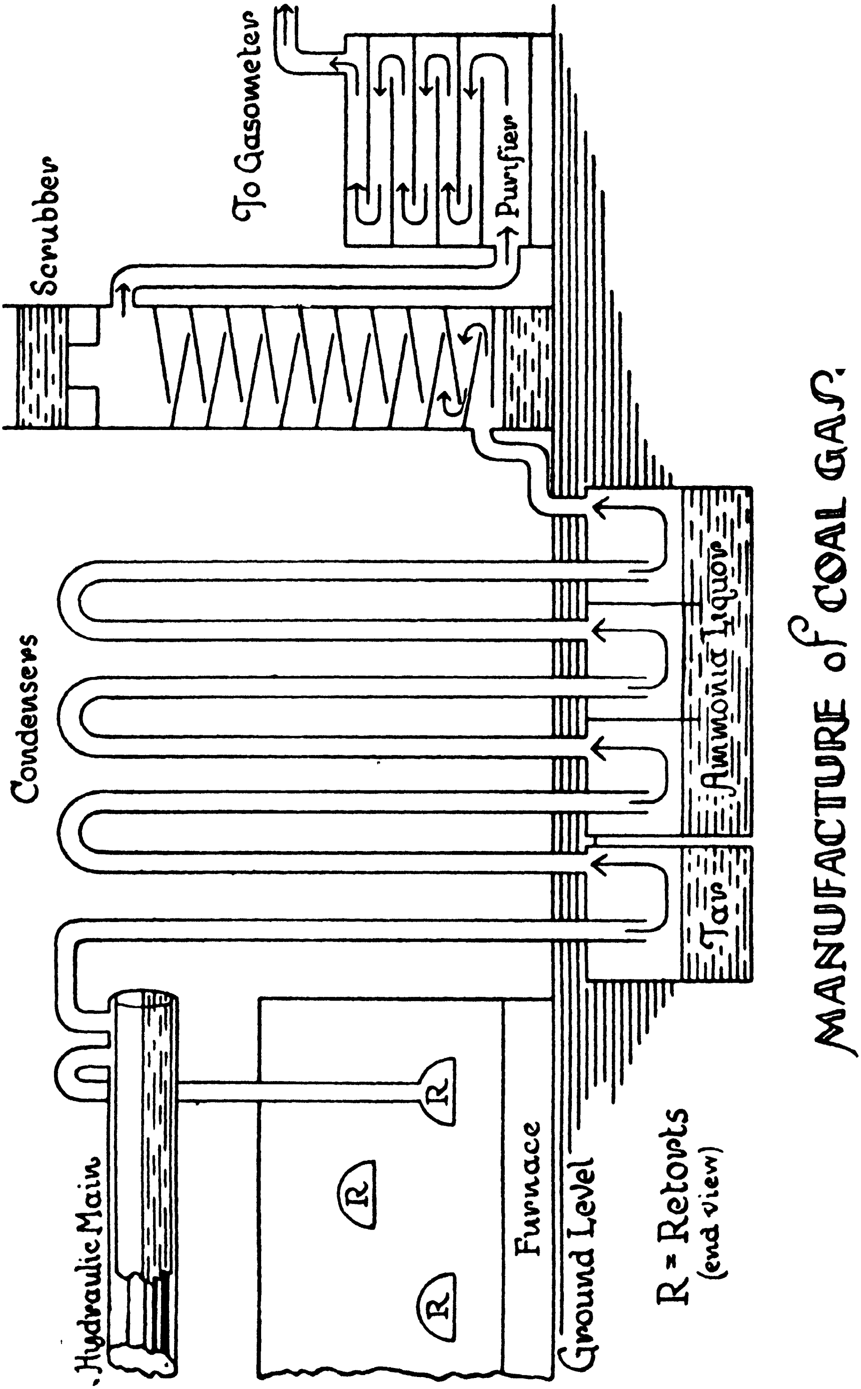

MANUFACTURE of COAL GAS
Hydraulic Main
Condensers
Scrubber
To Gasometer
Purifier
Ammonia Liquor
Tar
Furnace
Ground Level
R
R
R
R = Retorts
(end view)

FIG. 27

practice to blow steam through the gas retorts after the carbonisation of the coal and to mix the gases obtained—principally carbon monoxide and hydrogen—with the coal gas. The mixture, although it has less illuminating power, has a higher calorific value than coal gas alone. Since gas is now mainly used for cooking and heating, this is a decided advantage. Experiments have also shown that if a small quantity of oil be introduced into the retort before passing the steam, higher yields of gas with a greater calorific value are obtained.

Coal gas consists chiefly of hydrogen, carbon monoxide and the hydrocarbon methane, or marsh gas (CH_4). It contains in addition small amounts of the hydrocarbons acetylene (C_2H_2), ethylene (C_2H_4) and benzene (C_6H_6), and traces of carbon dioxide, nitrogen and oxygen. Hydrogen and carbon monoxide burn with a non-luminous but hot flame, and they are responsible for most of the heat produced by the combustion of coal-gas. Methane burns with only a slightly luminous flame; ethylene, acetylene and benzene, however, burn with a very luminous flame and confer upon coal gas its illuminating properties. The luminosity of a coal gas flame depends upon the preferential combustion of the hydrogen in the hydrocarbons, and the particles of carbon set free glow or become incandescent in the burning hydrogen. In other words there is a race for the oxygen of the air between the carbon and hydrogen of the hydrocarbons, and the hydrogen being the fleeter of the two, gets there first and is burnt to water vapour. The particles of carbon which separate, rise in the hydrogen flame, become incandescent at the high temperature and combine with the oxygen of the air surrounding the mantle of flame to form carbon dioxide. If coal gas be mixed with air before burning, the carbon particles are completely burnt away and the flame becomes non-luminous, but gives out more heat since the rate of oxidation is more rapid. This is what happens in the Bunsen burner and in the domestic gas burners used for cooking and heating. Gas passes from the mains through a jet surrounded by a wider tube, at the base of which are holes through which air is drawn by the upward rush of the gas. The gas mixes with the indrawn air and the flame obtained is non-luminous and suitable for heating purposes. If compressed air or oxygen is used instead of ordinary air an intensely hot flame is produced. Since a mixture of coal gas and oxygen is explosive, a special type of burner or blow-pipe is employed, in which a stream of oxygen is projected into the coal gas as it burns at the mouth of a tube.

As a domestic fuel, coal gas has managed to hold its own. As an illuminant it would have been almost obsolete by to-day but for an ingenious invention by Auer von Welsbach of Heidelberg. In 1884 he showed that the oxides of some of the rare metals give out an intensely brilliant light when raised to incandescence, and after many trials he found that the best results were obtained with a mixture of 99 per cent thorium oxide and 1 per cent cerium oxide. In spite of constant research on the subject no other known mixture has given such satisfactory results. From Auer's researches the modern incandescent gas mantle has evolved. The thorium and cerium used in its manufacture are extracted from the mineral known as monazite sand, which is found in Brazil and Travancore, India. The old type of mantle was made from ramie-fibre, soaked in a solution of cerium and thorium nitrates, containing a little beryllium nitrate to toughen the finished product. The mantle was then ignited to burn off the organic matter of the fibre and the skeleton remaining strengthened with collodion, which was burnt off just before use. Gas mantles are now made by dipping a fabric of artificial silk, not vegetable fibre, into the same thorium and cerium solutions and they are not treated with collodion. Incandescent mantles are not only used in conjunction with coal gas, but also with "petrol-air gas", that is a combustible mixture of petrol vapour and air. This serves as an illuminant for country houses that are not supplied with coal gas.

Coal gas used to be sold at so much per cubic foot. Since nearly all gas-burners are now fitted with incandescent mantles and since gas is so widely employed as a fuel, it is now sold according to its heating power, which is measured by the *therm.* This is a far more satisfactory standard as the consumer is paying for the heat energy he receives. A therm is 100,000 British thermal units (B.Th.U's.), or the amount of heat required to raise the temperature of 100,000 lbs. of water through 1° Fahrenheit. A good quality gas should have a heating value of 4·5 therms per 1,000 cubic feet. This means that 1,000 cubic feet of gas on combustion produces enough heat to raise the temperature of 450,000 lbs. of water 1° F.

Over 70 per cent of the potential efficiency of coal is wasted in the average household grate and 25 to 75 per cent in industrial plants. Attempts have been made to increase the efficiency of coal by burning pulverised coal. If powdered coal be blown into furnaces the surface of the coal exposed to the air is increased and combustion is more rapid and efficient. Moreover, the air supply can be regulated and losses due to the escape of hot gases can be minimised. By using special burners a mixture of pulverised coal and air can be burnt at a jet. The advantages of this method are that no stoking is required since the pulverisation and conveyance of the coal to the furnace is mechanical, low grade coals can be used, and less fuel is required since combustion is more complete. It is claimed that pulverised coal is cheaper than oil and since 1920 the use of this form of fuel has undergone rapid development especially in steamships, locomotives and in metallurgical works. A hundred and fifty million tons of pulverised fuels are used per annum.

When raw coal is burnt in an open grate or in factory furnaces, gas and tarry products are produced, and these on incomplete combustion give rise to carbon in the form of smoke and soot. Not only does this result in the loss of such valuable by-products as coal-tar and ammonia, but the atmospheric pollution (*see Plate* 20) due to smoke seriously affects health. The acid gases which accompany the soot and smoke pass into the air and have a destructive effect on vegetation and stonework. Smoke and soot cut out the health-giving ultra-violet rays from the sun and are responsible for the black fogs that commonly occur in large towns. Experts have calculated that the deposit of soot in London annually amounts to the weight of half the population. According to another calculation 2½ million tons of soot are annually deposited in the British Isles. In some industrial districts, e.g. Oldham, over 500 tons of soot per square mile are deposited during the winter months. This represents an enormous wastage of fuel, impairs the health of the population and increases the cost of decorating and painting and laundry bills;

Manchester alone spends on washing bills £250,000 a year more than would be necessary in a soot-free town. During the combustion of coal the small amounts of sulphur that it contains are oxidised to sulphur dioxide, which passes out into the atmosphere and causes destruction of stonework and brickwork. Over half a million tons of sulphuric acid are annually discharged into London air by the combustion of coal! Soot may hold from 4 to 8 per cent of free sulphuric acid. In Manchester £750,000 worth of damage is caused every year by smoke; this and the extra laundry bills mean an increased expenditure of £1,000,000 per annum for only one town of 800,000 inhabitants. Increased use of gas and electricity is one immediate solution of the smoke problem and there is no reason why atmospheric pollution should not be prevented, in the case of large factories at any rate, by washing the furnace gases before they escape into the air. This would remove the harmful acid gases (sulphur dioxide) and the soot produced by the combustion of coal. The super-power station in course of erection at Battersea by the London Power Company is to be fitted with a gas-washing plant to prevent soot and acid gases getting into the air.

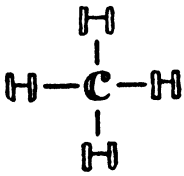
Apart from the smoke nuisance the economical utilisation of coal is an important national and scientific problem for this country. Coal is the nation's life blood and during the last hundred years some 50 per cent of it has flowed in vain. Our coal supplies will not be everlasting and we must use them in the most economical way. Extensive electrification and gas heating would ensure the conservation of the valuable by-products of coal which at present go up the domestic and factory chimney, and at the same time would do much to eliminate the smoke evil.

Attempts have been made to produce a smokeless fuel from coal by what is known as *low temperature carbonisation*. In gas works coal is carbonised at about 1,000° C., that is at relatively high temperatures. But the coke obtained by this process is not suitable for use in open grates. If coal be carbonised between 500° C. and 600° C. the residual coke, or rather semi-coke, can be burned in domestic grates without producing any smoke; it still retains enough gas-forming substances to make it inflammable. Quantities of this special low-temperature coke have been put on the market under the name of coalite, semi-coke and gloco. The calorific value—13,500 B.Th.U.'s—is considerably lower than that of coal. The amount of gas, benzene and ammonia obtained by the low temperature carbonisation of coal is considerably less than that obtained by carbonising it at 1,000° C., as in the gasworks. Only about half the volatile material is driven off by carbonising coal at 500° C. Increased quantities of tar and oils are produced in the low temperature process, and although the *volume* of gas is smaller than that obtained by high temperature carbonisation, it is much richer and has a greater calorific value. The tar, which is totally different from that obtained in gas-works, can be worked up for motor spirit, lubricants and fuel oil. The development of the low temperature carbonisation industry in this country and elsewhere has been very slow because the by-products of high temperature carbonisation—gas, tar, pitch, benzene and ammonia—have a ready market and are used as sources of some of the most important chemicals. For the industry to be profitable the semi-coke obtained must be sold at a price slightly above that of coal, and it is certain that it will be difficult to persuade the average housewife to pay more for semi-coke with a calorific value of 13,500 B.Th.U.'s than for coal with a calorific value of nearly 15,000 B.Th.U.'s The public do not realise that the ordinary methods of heating by coal are wasteful and bad for health. Nothing short of a law prohibiting the use of raw coal in open grates will solve the problems of smoke abatement and the economical utilisation of coal.

The coal used for low temperature carbonisation is chiefly in the form of slack or dust. In America *double carbonisation* has been recently introduced. Coal is first subjected to low temperature carbonisation to obtain a high yield of tar and oils, and the solid residue is briquetted and subjected to high temperature carbonisation to secure the ammonia and benzene compounds that are not obtained in the previous process. The many advantages of low temperature coal carbonisation will be obvious to the reader. If all coal were carbonised before burning there would be less atmospheric pollution, resulting in improved health to town dwellers and less destruction to property. The volatile substances that normally pass up the chimney would be conserved to produce motor spirit and fuel oil. Valuable oils are contained in the tar formed during carbonisation and these can either be used for raising steam, for internal combustion engines, or for the production of petrol. The light spirit obtained can be used in cars or mixed with petrol; it has "anti-knock" properties. In addition, the tar acids, which include phenols and cresols, are valuable. Phenol, or carbolic acid as it is commonly called, is used in the manufacture of antiseptics, dyes, aspirin and explosives; the cresols are employed for creosoting timber, for the preparation of sheep dips, disinfectants, bakelite and synthetic resins.

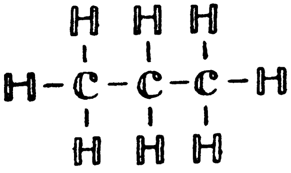
In addition to coal, nature has supplied us with a liquid fuel known as petroleum or rock oil, the existence of which was recognised by fire worshippers many centuries before Christ. Herodotus and Pliny, two classical writers, mention its occurrence in Asia and its use, to a very limited extent, as an illuminant. The destruction of Sodom and Gomorrah, which were situated in an oil bearing region, has been attributed to a huge oil fire, the oil being set free by some subterranean disturbances. The ancients, and more recently the American tribes, used small amounts of petroleum medicinally. In 1857, the first oil well was bored at Titusville, Pennsylvania, by an American engineer. He was in fact the first to "strike oil". At one time the Pennsylvanian oil-fields produced most of the world's oil, but oil-fields have now been opened up in Oklahoma, Texas, California and in Russia, Persia, Rumania, the Dutch East Indies, Burma and Mexico. The rapid development of the petroleum industry has been caused not only by the extensive use of petroleum products as illuminants and lubricants, but also by the increased demand for light oil fuel in the motor and automobile industries. In America alone 8,000,000 gallons of motor spirit are consumed annually. The world's annual production of petroleum is about 142,000,000 barrels and of this the American wells supply 70 per cent.

Crude petroleum is a heavy, thick, greenish-brown oil consisting, in the case of American petroleum, mainly of hydrocarbons which are of the saturated type, that is all the carbon atoms have united with the maximum number of hydrogen atoms. These saturated hydrocarbons are known as paraffins, the simplest member being methane or marsh gas. A molecule of methane contains one atom of carbon united to four of hydrogen:



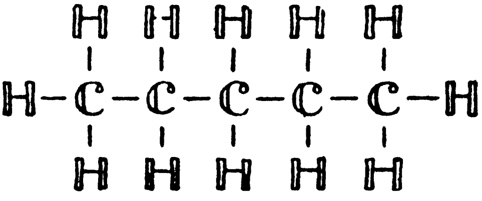
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Since an atom of carbon never combines with more than four atoms of hydrogen, the carbon is said to be saturated. The *natural gas* which escapes from petroleum wells consists of more than 90 per cent methane. In America natural gas is used in place of coal gas for lighting and heating. A supply of natural gas was discovered in 1893 at Heathfield in Sussex, and it is used in the neighbourhood to the extent of 1,000 cubic feet per day. Carbon has the remarkable property of linking up with other atoms of carbon to form "chains" of carbon atoms, thus:



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

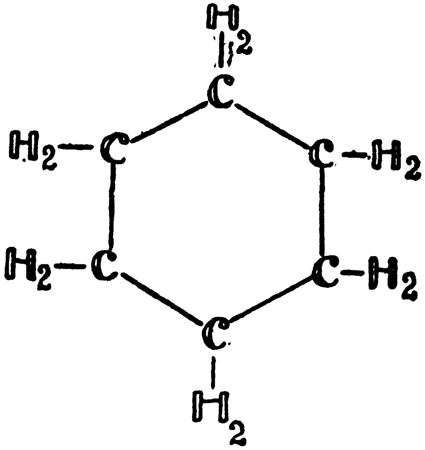
C_3H_8 (Propane)



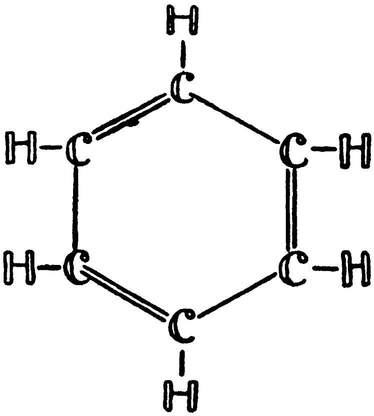
$$\begin{array}{ccccccccccc} & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & - & C & -H \\ & | & & | & & | & & | & & | & \\ & H & & H & & H & & H & & H & \end{array}$$

C_5H_{12} (Pentane)

American petroleum consists chiefly of hydrocarbons of this type (from CH_4 up to $C_{30}H_{62}$). Russian petroleum on the other hand contains hydrocarbons belonging to another series, termed *naphthenes*. In these compounds the carbon atoms are joined in the form of closed rings:



In benzene (benzol) the carbon atoms are also arranged in a ring:



Benzene is present in the petroleum found in Borneo, Persia and Burma. The petrol fraction obtained by distilling Borneo oil contains 40 per cent of it.

Very little is known with certainty about the origin of petroleum. The most likely explanation is that it has been formed by the gradual decomposition of the remains of marine animal and vegetable life under the influence of high temperatures and pressures. The Russian chemist, Mendeléeff, supposed that the hydrocarbons of petroleum were produced by the action of water on the carbides of metals within the earth. It is well known that metallic carbides—compounds of carbon with the metals—are decomposed by water, the carbon of the carbide uniting with the hydrogen of the water to form a hydrocarbon. Calcium carbide, for example, forms the hydrocarbon acetylene when it reacts with water. It is possible that water, penetrating the thin crust of the earth, has acted upon subterranean metallic carbides to produce the mixture of hydrocarbons that we term petroleum.

In order to separate the various constituents of petroleum the crude oil is pumped from the oilfields through pipes to the refineries (Plate 22) where it is distilled in large boilers or retorts. Since the different constituents have different boiling points they can be separated by distillation. The liquid distilling over between 40° C. and 70° C. is known as petroleum ether and is used as a solvent and as a local anæsthetic. Gasoline or petrol distils over between 70° C. and 120° C. It is used as motor spirit and mixed with air for producing "air-gas", which is employed in illuminating country houses. Petroleum benzene or benzoline, used for dry cleaning and as a solvent, distills between 120° C. and 150° C. Kerosine or burning oil (paraffin oil) comes over between 150° C. and 250° C., and fuel oil or gas oil distills between 250° C. and 350° C. It is used in Diesel engines and for increasing the calorific value of coal gas. The higher boiling fractions, which are distilled in a current of superheated steam in many refineries, include oils used for lubrication—light and heavy lubricating oil—and for combustion in furnaces. The fractions of highest boiling point yield vaseline and paraffin wax, the latter being used for making candles and waterproof paper, for insulation in electrical work, and for coating metals to prevent rusting. Paraffin wax is also produced by the distillation of shale, brown coal, and large quantities of it occur naturally in Galicia in the form of a mineral wax termed *ozokerite*. After the separation of these various products from petroleum the residue which remains is known as bitumen or asphalt. It is used for road making and roofing.

The use of oil as a fuel has increased to a remarkable extent during the present century, and with the rapid development of the petrol engine the demand for the lighter oils (petrol, gasoline) has threatened to exceed the supply. The heavier petroleum bodies are totally unsuitable for use in motor spirit as they produce carbon in the engine cylinders, which thereby become fouled. It was not so long ago that the refiners wanted to get all the kerosine and lubricating oils that they could out of petroleum; the petrol or gasoline and the lighter oils had little use except as solvents. Now the position is reversed. The 25 per cent of light oils obtained by distilling petroleum is insufficient to meet the demands of the motor and aeroplane industries. This is remedied by mixing the heavier oils with the lighter ones and by "cracking" the heavier petroleum oils. In the cracking process the oils are heated under pressure in the absence of air to a fairly high temperature, with the result that the larger hydrocarbon molecules split up and yield the simpler ones that are present in gasoline. Heating the heavier oils with aluminium chloride facilitates their breaking down to the lower oils. Owing to the decreased consumption of kerosine for illuminating purposes, large quantities of this oil are "cracked" to yield lighter fuel oils suitable for use as motor spirit. The oil so obtained contains unsaturated hydrocarbons[1] and hydrocarbons of the benzene type (benzene, toluene), and it has the valuable property of preventing "pinking" or "knocking" (i.e. detonation) in motor engines. Petrols containing large amounts of the paraffin hydrocarbons are liable to cause "knocking", but this objectionable property can be removed either by adding benzene, the product then being known as *benzol mixture,* or by adding small amounts of suitable dopes such as lead tetraethyl, $Pb\ (C_2H_5)_4$. In the latter case the product is known as *ethyl petrol.* Ethylene dibromide, $C_2H_4Br_2$, is added to the mixture in order to convert the lead, which would otherwise deposit on the sparking plug points, into a volatile lead salt (lead bromide) and chlorinated naphthalene (halowax oil) is also added as a valve lubricant. Ethyl petrol is coloured red for purposes of identification. In Germany iron carbonyl—formed by the action of carbon monoxide on iron—is used to prevent "knocking".

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[1] Unsaturated hydrocarbons contain less hydrogen than the saturated hydrocarbons.

When petrol or gasoline is used as a source of power in internal combustion engines, e.g. in aircraft and motor vehicles, the suction stroke of the engine sucks the petrol through the carburettor jets and it is transformed into vapour which becomes mixed with air. The chemical energy of the combustible mixture of air and petrol vapour becomes converted into mechanical energy. The petrol-air mixture is compressed in the cylinders by the compression stroke of the piston and then ignited by a spark from the sparking-plug. Since the products of combustion occupy a larger volume than the petrol-air mixture, and since the combustion is attended by a rise in temperature a large increase in volume and hence pressure result. If the engine is to run smoothly the pressure should be communicated to the piston in a regular and not explosive manner. Up to a certain point increased compression of the petrol-air vapour mixture increases the efficiency with which the energy produced by combustion can be converted into mechanical energy. But with all fuels "pinking" or "knocking" occurs above a certain degree of compression, because the petrol-vapour and air mixture ignites with a shattering explosion and sends the piston hurtling down the cylinder, in a manner similar to that of a sharp blow from a hammer. This causes stresses on the engine parts and loss of power. Benzene and alcohol can stand greater compression than other liquid fuels, and in the case of alcohol the increase in the efficiency of the engine with compression more than compensates for its lower calorific value. Although the calorific value of alcohol is 10,350 B.Th.U.'s per lb. and that of petrol 18,600 B.Th.U.'s a heating efficiency of 30 per cent is possible in the case of the former fuel. The maximum efficiency obtainable with petrol is 20 per cent. When the oil-wells are dry, when coal becomes a museum exhibit, and when our peat bogs are exhausted, alcohol will be our only important fuel other than wood. Alcohol will be the fuel of the future. Vast quantities of potatoes, rice, wheat and beetroots will be grown to obtain it, unless of course it can be obtained from cheaper sources. By fermenting these crops under suitable conditions the starch that they contain may be converted into sugar and finally into alcohol. At present petrol is so cheap that alcohol cannot compete with it as fuel.

Oils similar to those of petroleum can be obtained by heating the bituminous oil-bearing rocks known as *oil shales.* Ever since 1850 a flourishing oil industry has existed in Scotland by the distillation of shale. On an average a ton of European shale yields 23 gallons of crude oil, from which on further distillation combustible gas, lubricating oils and motor spirit may be obtained. American shales yield as much as 30 gallons of oil per ton. In addition, shale yields considerable quantities of ammonia. Important fuel and lubricating oils are also obtained in the low temperature carbonisation of coal and lignite, and by the high temperature carbonisation of coal, as practised in the gas-works, benzene is obtained. Owing to its anti-knock properties it is blended with petrol for use as a motor fuel.

The petrol obtained from crude petroleum is a mixture of hydrocarbons, in which the amount of hydrogen present per given weight of carbon is approximately twice what it is in coal. A highly successful process for the conversion of powdered coal into oils resembling those obtained from petroleum has been perfected by the German chemist, F. Bergius. If coal differs from petroleum mainly in its hydrogen content, it is reasonable to suppose that a product resembling petroleum might be obtained by heating coal with hydrogen, preferably under pressure since hydrogen is a gas. This is the principle of Bergius' process, or *Berginization* as it is now called. Powdered coal is mixed with a little alkaline iron oxide and bound with a suitable tar or oil; it is then heated with hydrogen to 400° C. under a pressure of 200 atmospheres. We have seen that coal contains some 5–6 per cent of oxygen. Part of the hydrogen combines with this unwanted oxygen—there is no oxygen in petroleum oils—to form steam, and the remainder is taken up by the carbon of the coal to form liquid hydrocarbons. At the same time a small quantity of the hydrogen combines with nitrogen present in the coal to form ammonia. The crude oil that results is distilled to yield motor spirit, fuel oils, Diesel oil and lubricating oil. About 50 per cent of the coal is converted into oil and 20 per cent into combustible gas. The Interessen Gemeinschaft of Leuna, Germany, are producing oil from coal by this method and factories are in course of erection in this country for the same purpose. If the process could be worked successfully in Great Britain we could ourselves manufacture the £40,000,000 of oil that is imported annually, and the price of petrol would drop to *7d.* per gallon.

Over 100,000 tons of hydrogen are used per annum for hydrogenating coal. Most of it is made by the Bosch process, in which water gas, a mixture of hydrogen and carbon monoxide, is passed with steam over heated iron oxide. The latter acts as a *catalyst* or accelerator. Steam is composed of hydrogen and oxygen, and the latter attaches itself to the carbon monoxide to form carbon dioxide, thereby leaving hydrogen gas. This is separated from the carbon dioxide by washing with water and caustic soda in steel towers; the carbon dioxide is absorbed and leaves hydrogen. Hydrogen is also produced technically by blowing steam through heated iron contained in vertical retorts.

The manufacture of cheap motor fuel from coke has been developed by Fischer in Germany. By passing steam over red-hot coke a mixture of carbon monoxide and hydrogen gas is obtained (water gas). Fischer and his collaborators have shown that these gases can be made to combine in the presence of a suitable catalyst or activator, and under suitable conditions of temperature and pressure, to yield, among other products, methyl and ethyl alcohols; the latter is ordinary alcohol. The mixture is known as *synthol*. More recently Fischer and Tropsch discovered that if the process be carried out without the use of pressure, liquid and solid hydrocarbons are formed, similar to those occurring in petroleum. The liquid oils yield considerable quantities of motor fuel and fuel oils suitable for combustion in furnaces.

The use of oil as a fuel for furnace combustion has greatly increased during the last few years. Fuel oil has a calorific value of nearly 20,000 B.Th.U.'s per lb.; the corresponding figure for the best anthracite is 15,750. Apart from its higher calorific value, oil is lighter than coal, occupies less space, requires no labour for stoking, and is cleaner and safer. There is no possibility of fires in the coal bunker with oil fuel. The rapid development of the use of oil fuel on ocean liners will be evident from the fact that about 40 per cent of to-day's tonnage is equipped to burn oil. For furnace combustion the oil enters the furnace in the form of a fine mist or spray and a sufficient air supply is maintained for the fuel to burn smokelessly.

The convenience of gaseous fuels for industrial purposes has led chemists to investigate the production of these from coal and coke. We have already dealt with coal gas and we have seen that if steam be blown over red-hot coke, there is produced a mixture of carbon monoxide and hydrogen known as water gas. Slack coal is sometimes used in place of coke. Water gas burns with a non-luminous flame, and although valuable industrially for heating, it is useless for lighting purposes. Since it has a high calorific value it is generally added to coal gas. If required for illumination it is either enriched by adding *gas oil* from petroleum or *carburetted* by passing it through heated brickwork towers into which oil is sprayed. The oil is vaporised and "cracked", to form gaseous hydrocarbons capable of burning with a luminous flame, and these became mixed with the water gas (Fig. 28). A gas called illuminating gas, and sometimes by courtesy "coal gas", is a mixture of 50 to 70 per cent carburetted water gas and coal gas. When water gas is burnt from a special burner a short, hot flame is obtained and this is utilised in welding and melting steel. Fuel gas for use in factories or for gas engines is also obtained by passing air through deep beds of red hot coke. The resulting gaseous mixture, known as *producer gas*, contains mainly carbon monoxide (30 per cent) and nitrogen (65

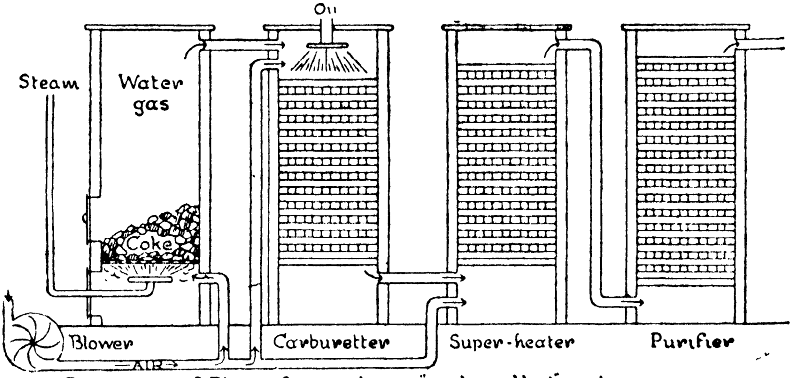


Diagram of Plant for making "carburetted" water gas.

FIG. 28 [From Partington's *Everyday Chemistry*.

per cent), and although its calorific value is not very high it is cheap. The hot gases are burnt by admitting more air, when the carbon monoxide burns to carbon dioxide. Producer gas is used in steel smelting furnaces of the Siemens type (p. 123). Semi-water gas, or Dowson gas, is produced by combining the operations for making producer gas and water gas, i.e. by passing a mixture of air and steam over incandescent coke. It has a calorific value one and a half times as much as that of producer gas, and is used for steam raising, for the production of power by internal combustion engines and for metallurgical processes.

Considerable economy in the combustion of fuel has been effected by the application of what is known as "surface combustion". As far back as 1817 Davy discovered that a warmed platinum filament introduced into a non-explosive mixture of air and coal gas gradually became incandescent, and at the same time the coal gas was gradually burnt up without the poduction of a flame. In other words the platinum accelerated the combustion of the coal gas. Before a combustible mixture of gases can burn it must be heated up to a certain temperature,

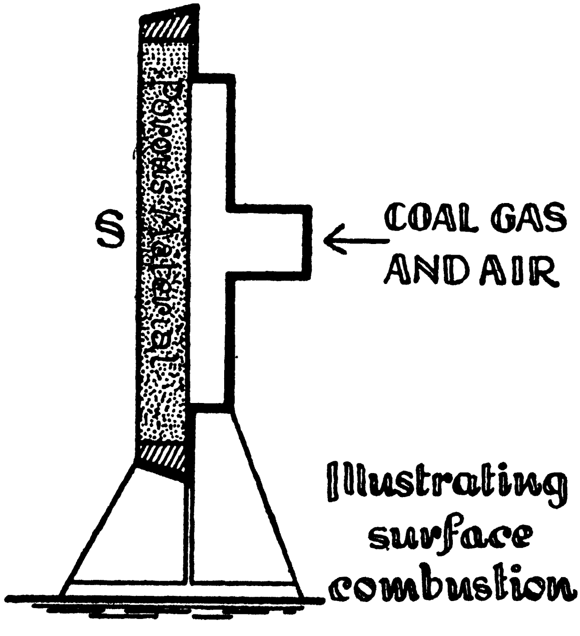


FIG. 29

called the *ignition temperature*. But platinum and many other substances can accelerate the combustion of gases below the ignition temperature by virtue of what is called "surface action". As Faraday explained nearly a century ago the reacting gases—say coal gas and air—are "condensed" or taken up by the surface layer of the platinum and so brought into closer contact, with the result that they react more readily. Combustion is therefore more rapid. Professor Bone, of the Imperial College of Science and Technology, made important studies on this surface effect. His first investigations go back to 1887. He showed that all solids, not only platinum, show this surface action and accelerate the combustion of gases below their ignition temperature, although the degree of acceleration depends upon the nature of the solid. Bone found that when solid substances are heated to incandescence they all possess this property of accelerating gaseous combustion to much the same degree. He applied the results of his researches to increasing the efficiency of various industrial heating appliances, such as gas furnaces, gas cookers and heaters.

This "surface combustion" can be utilised in gas heaters by passing a mixture of air and coal gas through a porous mass of heat-resisting or refractory material (fireclay, alumina, etc.). The mixture is ignited on the exit surface (S in Fig. 29) and flameless combustion occurs in the surface layers of the porous matter, which gradually becomes incandescent and emits much heat. Cooking vessels placed over the heat-resisting material are heated up in half the time taken over a naked gas flame. When using an ordinary gas flame for heating purposes, the flame in immediate contact with the heated object is put out and escapes up the chimney. During surface combustion the whole of the gas is burnt and 90 per cent of the heating value of the gas is utilised. Surface combustion can also be applied in the firing of boilers, the tubes of which contain fire-resisting material. A saving of 15 per cent in the fuel costs can thereby be effected.

CHAPTER VIII

THE NITROGEN PROBLEM

NITROGEN, the gas that constitutes roughly four-fifths of the atmosphere, is an essential constituent of all animals and plants. It enters into the composition of that important class of foodstuffs, the proteins, from which the body tissues of animals and plants are built up. The proteins are complicated organic substances containing carbon, hydrogen, oxygen, nitrogen and occasionally sulphur and phosphorus. Animals derive the nitrogen of their tissue proteins either by feeding on other animals or on plants. All animal life, however, is ultimately dependent upon plant life, for although some animals feed upon other animals, these must eventually feed upon plants or plant products. In spite of the enormous supplies of gaseous or free nitrogen in the air, very little of this is consumed by plants in the building up of their proteins. Most of them obtain their nitrogen, not from the air, but from nitrates and other nitrogen compounds in the soil, which they elaborate into proteins. On the death and decay of the plant these pass into the soil. If, however, the plant is eaten by an animal, its proteins are digested and eventually form part of the tissue protein of the animal. But during the life of the animal these proteins undergo constant breakdown and renewal, and in the process a certain amount of organic nitrogenous waste products result. These are excreted mainly in the form of the organic compound urea and eventually find their way into the soil. The nitrogen absorbed by plants from the soil is thus eventually returned to it either on their death and decay or through animals. But the organic nitrogen compounds returned cannot be used again as such by plants; the majority of these can only assimilate nitrogen in the form of nitrates, although recent research has shown that many green plants may, under certain circumstances, use the nitrogen from the air. Fortunately there exist in the soil microscopic organisms termed bacteria, some of which decompose organic nitrogenous matter with the liberation of ammonia, and this substance is successively converted into nitrites and nitrates by what are termed the nitrifying bacteria. The nitrates consumed by plants are thus eventually re-formed.

This nitrogen cycle is modified to some extent by the action of certain soil bacteria and by man himself. There are some bacteria that bring about denitrification in the soil, that is, they convert soil nitrates into gaseous nitrogen, which escapes into the air and is thus lost. Much of the organic nitrogenous matter excreted by town dwellers never finds its way into the soil to replace that which is taken from it. In many large towns this nitrogenous waste is diverted into the sea as sewage, or else treated to render it innocuous and then discharged into rivers. This means that practically the whole of the nitrogen from the food consumed is irrecoverably wasted. Civilised man is in fact rapidly transferring his combined nitrogen indirectly into the sea. If we assume that the population of Great Britain is 45,000,000, the amount of urea excreted annually corresponds to two million tons of ammonium sulphate—four-fifths of the world's annual production—or to 1,350,000 tons of sodium nitrate. A small quantity of the excreted nitrogen reaches the soil and some of it is utilised on sewage farms, where it is distributed over the land. In 1913, 13,000 tons of ammonium sulphate were produced from sewage in France, although this dropped to 5,000 tons in 1917. New methods of sewage disposal have been introduced in Germany, U.S.A., and some of the inland cities of this country (Birmingham). The sewage is allowed to settle and the sludge utilised for the production of power gas and nitrogenous fertilisers (p. 322). Large towns near the sea dispose of their sewage by pumping it into steamers, which dump it at a safe distance from the land. This method is used by the London, Glasgow and Manchester authorities.

Certain plants belonging to the *Leguminosae* family, which includes peas, beans and clover, have the power of utilising the nitrogen of the air. It is fixed for them in the form of nitrates by bacteria that dwell in the minute nodules, or bulb-shaped protuberances, on the roots of the plants. The nodules are in fact miniature nitrogen factories in which the bacteria make nitrates far in excess of their own requirements, and not only pass on to their host plant what they do not want themselves, but also enrich the surrounding soil with fixed nitrogen available for plant consumption. For this reason leguminous crops are sown by farmers and dug in as fertilising agents. Nature effects the enrichment of the soil with nitrates in yet another manner. The gigantic electric discharges occurring during thunderstorms cause some of the atmospheric nitrogen and oxygen to combine, and the oxides of nitrogen produced are washed by rain into the soil, where they form nitric acid and nitrates. It is estimated that 250,000 tons of nitric acid are formed daily in this way; this means that every acre of ground in this country is enriched annually with 11 lbs. of combined nitrogen. By taking a leaf out of nature's book man has succeeded in making the nitrogen and oxygen of the air combine to form oxides of nitrogen, and from these he has obtained nitric acid and nitrates. We must also remember that man adds large quantities of nitrogen compounds to cultivated soil in the form of fertilisers or artificial manures. These may consist of inorganic nitrates and ammonium compounds, or organic nitrogenous matter in the form of dried blood, cotton seed meal, fish scrap, leather scrap and animal excreta.

Important as nitrogen is to animal and plant life, the free or gaseous element is comparatively useless. It is fixed or combined nitrogen that we want—nitrogen combined with other elements to form food proteins, nitrates and fertilisers. Although we are constantly breathing it in we cannot use it directly as food. Our bodies need the element in a combined state, and unfortunately for us foods rich in combined nitrogen are the most costly. We must pay, say, eighteen pence a pound for meat, which never contains more than 4 per cent nitrogen, in order to get enough nitrogen to live on, and those who are vegetarians find certain nitrogenous foods (nuts) more costly still. Combined nitrogen also forms an essential constituent of dyes, such as indigo and the aniline dyes, and of many drugs and explosives; and its compound with hydrogen in the form of ammonia is used in the manufacture of soda and, in the liquid condition, for the purposes of refrigeration. Cyanides, which also contain combined nitrogen, are employed in the extraction of gold and in electro-plating. But the principal application of combined nitrogen is in the production of food. The application of nitrogenous fertilisers to cultivated soil means increased crops, more fertile pasture land, and hence more live-stock from a given area under cultivation.

Until comparatively recently the vast supplies of atmospheric nitrogen have gone untapped. Man has been content to rely upon natural nitrate deposits and upon coal for his combined nitrogen. The large deposits of potassium and sodium nitrates that occur in Chile and India are used directly as nitrogenous fertilisers, or else converted into nitric acid. This important article of commerce is required in the manufacture of gun-cotton, dynamite, T.N.T., blasting gelatin, cordite, celluloid, dyes, collodion, lacquers, artificial silk, leather, gas mantles, imitation ivory, certain drugs, fireworks and laughing gas; it finds employment in engraving, calico-printing and metallurgy. The extensive nitrate deposits in Chile extend over about 500 square miles, corresponding to a yield of 4 million tons of crude nitrate per square mile. In India and the East saltpetre results from the action of bacteria on deposits of animal refuse, the nitrogen of which is converted into the nitrates of potassium and calcium.

Coal contains small amounts of nitrogen, as well as from 5 to 6 per cent of hydrogen, and when the coal is distilled in the gas works these two elements combine to form ammonia; this is subsequently converted into ammonium sulphate by treatment with sulphuric acid. Coals used for gas manufacture contain about 1½ per cent of nitrogen, which corresponds to a theoretical yield of 160 lbs. of ammonia sulphate per ton of coal. In practice the amount seldom exceeds 30 lbs. per ton, although it has been stated that by passing steam over the residual hot coke increased quantities of ammonia can be produced. Appreciable quantities are obtained as a by-product from coke ovens, blast furnaces, and producer-gas plants, the ammonia being derived from the coal used. Peat contains much nitrogen, and many processes are either worked or are proposed for transforming this nitrogen into ammonium sulphate. By the partial carbonisation of peat not only ammonia, but power or producer gas can be obtained, and there is no reason why peat carbonisation should not develop into a profitable industry. There are over 20,000,000 tons of undeveloped peat in the U.S.A., while large reserves exist in Ireland, Finland, Russia, Canada and Germany. One ton of dry peat yields 88 lbs. of ammonium sulphate. Large amounts of ammonia are recovered in Scotland by the distillation of bituminous shale. Ammonium sulphate is a valuable fertiliser, and ammonium nitrate is a constituent of some explosives. Guano, formed from the excrement and carcases of sea birds, is highly nitrogenous, and finds considerable use as a fertiliser, although the South American product is rapidly becoming exhausted.

The important connection between combined nitrogen and our daily bread will be apparent from the following figures. Ordinary unmanured soil gives an average yield of 12·7 bushels of wheat per acre; on manuring with nitrates this can be increased to 40 bushels per acre. But if the whole of the world's wheat supply came from unmanured ground there would not be enough wheat to feed us all. The increased crop, which means the difference between starvation and plenty, is made possible by the use of nitrogenous manures. It has been calculated that over 12 million tons of nitrates would be required annually to bring about this increased yield. As we have seen, our main natural sources of combined nitrogen are coal and the Chile nitrate beds. At the present rate of consumption our coal deposits may be exhausted in 200 years, and in any case coal supplies only a relatively small quantity of combined nitrogen. The by-products of coal cannot be relied upon to supply a nation with its combined nitrogen. The same is true of the nitrate deposits. If improved processes are used to work these, the amount of nitrates obtainable may amount to 250,000,000 tons, and at the present rate of consumption this would last a hundred years. Experts agree that in two hundred years our nitrate deposits in Chile and elsewhere will be depleted, an estimate that does not take into account the abnormal demand for combined nitrogen, which is roughly doubled every ten years. Since the chief application of combined nitrogen is in the production of food, man has been faced with what is known as the Nitrogen Problem, i.e. the problem of avoiding starvation by obtaining sufficient combined nitrogen for agricultural purposes.

In 1898 Sir William Crookes, then President of the British Association for the Advancement of Science, drew attention to the fact that the world was facing ultimate starvation, because under the existing conditions of heedless culture the wheat-growing lands were rapidly becoming exhausted of nitrogen. In the course of this address Crookes said:

> England and all civilised nations stand in deadly peril of not having enough to eat. As mouths multiply food resources dwindle. Land is a limited quantity, and the land that will grow wheat is dependent on difficult and capricious natural phenomena. . . . I hope to point a way out of the colossal dilemma. It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty.

Crookes' remedy for the shortness of wheat supply was the production and application to the soil of increased quantities of combined nitrogen, and he pointed out that since we are rapidly exhausting all the known sources of combined nitrogen we must look elsewhere for our supplies. The only promising source is the atmosphere.

Sir E. J. Russell has stated that an average of experiments spreading over sixty years shows that a yield of 12·7 bushels per acre from unmanured land could be increased to 23.2 bushels by the addition of manures containing 43 lbs. of combined nitrogen. According to Crookes 3,180,000 tons of combined nitrogen would have to be added to the soil annually to bring the wheat crop up to 20 bushels per acre. This is far in excess of the world's production of nitrates and ammonia.

The total consumption of wheat has become greater than Crookes anticipated because of the new consumers in Eastern countries, such as China and Japan. The number of acres under wheat at present is slightly below that which Crookes predicted would only feed the world until 1931, but the yield per acre has now been increased by 10 per cent. By the selective breeding of wheat to produce strains capable of resisting climatic extremes, the world's wheat areas have been considerably extended. The main increase in annual production is now to be looked for in the direction of intensive cultivation by the increased use of nitrogenous fertilisers. This increase must keep pace with the increase in the wheat-eating peoples. Crookes' warning, although somewhat premature, was well-founded. If our supplies of agricultural nitrogen are adequate, we have taken no account of the increased consumption of nitrogen compounds in industry, and for explosives in time of war.

Although chemists have long been aware that the air contains some 80 per cent nitrogen, this vast and practically inexhaustible supply remained untouched as a source of combined or fixed nitrogen until the beginning of the present century. In 1898 Crookes remarked:

> The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists. It is certainly deeply important in its practical bearings on the future welfare and happiness of the civilised races of mankind.

The nitrogen of the atmosphere over every square mile of earth weighs something like 20 million tons, or over thirty times the amount of the element present in the annual output of Chile nitrate and by-product ammonium sulphate. Without the air as a source of combined nitrogen the last war would never have continued for over four years. Nitrogen in the form of nitric acid is an essential constituent of all military explosives, and if Germany had been content to rely upon Chile nitrates as a source of nitric acid, hostilities would have soon ended. Germany did not have access to Chile nitrates; she was independent of them, having successfully solved the problem of fixing or combining atmospheric nitrogen before the outbreak of war. The consumption of combined nitrogen during the war exceeded the expectations of any nation, and there is no doubt that Ceres was stinted to pay Mars, with the result that people of many of the belligerent nations suffered from malnutrition. Nitrogen that should have been applied to the land in the form of fertilisers went to make explosives. During the early part of the war the Allies relied upon Chile nitrates as a source of combined nitrogen for explosives, but the submarine blockade instituted by Germany soon led to an alarming situation. Allied ships carrying Chile nitrate were sunk, and ships that should have carried food carried nitrates and explosives. Without Chile nitrates the Allies would have been forced to capitulate. The blockade showed that no nation can afford to depend upon a foreign source of supply for its combined nitrogen in time of war. It demands increased transport facilities at a time when a country can least afford it, and in the event of a successful blockade defeat through lack of munitions, or starvation, or both, is inevitable. In times of war the nitrogen supply should be adequate for both explosives and agriculture. The armies must be well-fed in addition to being well-equipped, and they must be supported by a well-fed nation. This means that war-time agricultural nitrogen must be in excess of the peace-time consumption.

Towards the end of the war France was successfully solving the nitrogen problem, and was well on the way to making herself independent of combined nitrogen from abroad. Most of the Allied nations made some contributions to the solution of the problem, although it is to be regretted that this country failed to do her share of the work. Our statesmen did not realise the scientific and national importance of the nitrogen question. Their sublime ignorance is revealed by the fact that while Chile nitrates were being imported at great risk and expense, 60 to 70 per cent of our own combined nitrogen—ammonia—was actually exported, although it could have been used in the manufacture of explosives. At the same time, increased quantities of sulphuric acid were required for munitions, yet over half a million tons were exported between 1915 and 1916. We won the war in spite of our politicians. After the war had been on for some time, it was dimly comprehended in official quarters that combined nitrogen had some sort of use in war-time, and eventually research on nitrogen fixation was carried out by the Nitrogen Products Committee of the Munitions Inventions Department. The immense German Haber factory built at Merseberg for the preparation of synthetic nitrogen products was put up in under a year; even when Armistice was declared not a single British factory was fixing nitrogen. Just after the war, days were spent in the House of Commons debating the advisability of protecting "Key Industries," but those in authority did not realise that the nitrogen industry is the most important key industry of all. During the war we were fortunate enough to possess partial control of the Atlantic and to have access to Chile and to the Norwegian synthetic nitrogen products. Although the last conflict taught us the danger of relying on foreign countries for our combined nitrogen our rulers are still blind to the fact that the nitrogen problem is a national one, and they have left its solution to private enterprise. The Government factory at Billingham-on-Tees, erected for the preparation of synthetic ammonia, was abandoned in 1918 and sold to Brunner Mond and Co. Ltd. (now merged in Imperial Chemical Industries Ltd.). In 1924 24,000 tons of ammonium sulphate were produced, and at the present moment the output corresponds to 750,000 tons of ammonium sulphate per annum.

The position of the nitrogen industry in Germany during the war offers a sharp contrast to that in this country. Before 1914 Germany produced more ammonium sulphate than any other country and she was the biggest consumer of Chile nitrates. In 1913 she manufactured nitrogen products equivalent to 136,000 tons of nitrogen, and with imports consumed over 260,557 tons of combined nitrogen. The corresponding figures for this country are 99,800 tons and 54,000 tons respectively. In 1917 Germany increased her production of ammonium sulphate from 413,000 tons—the 1914 figure—to 700,000 tons, and manufactured large quantities of synthetic nitric acid. In 1914 she produced 60,000 tons of synthetic ammonium sulphate; this was increased in 1917 to 500,000 tons. Some millions of money were spent on the plant concerned. By oxidising her synthetic ammonia to nitric acid Germany was able to meet the military requirements of the Central Powers, which in 1917 were estimated to be 450,000 tons per annum. Her production of nitrolime (p. 203), which was 24,000 tons in 1913, expanded to 500,000 tons in 1917. The total production of combined nitrogen in Germany in 1913 represented 110,000 tons of nitrogen; in 1917 the total requirements represented 415,000 tons. The deficit of 305,000 tons was more than balanced by the manufacture of synthetic nitrogen compounds corresponding to 320,000 tons of nitrogen.

Nitrogen is a remarkable gas in that it is comparatively inert in the free state, but once it combines with other elements it displays exceptional activity. Because of the only slight affinity between nitrogen and the other elements that combine with it, many of its compounds are unstable and readily decompose with the production of heat and gas. On this account explosives are invariably nitrogen compounds.

Atmospheric nitrogen can be fixed or combined in a number of ways. Although Haber, one of the pioneer workers on the subject, once remarked that the fixation of nitrogen in the future for soil fertilisation would be through plant and soil bacteria, it is to electrical rather than to biological methods that man has turned. The fundamental discoveries on the fixation of atmospheric nitrogen were made by British investigators, but, as in the case of the dye industry, the results obtained have been industrially exploited by other countries, owing to the apathy and ignorance of those in authority at home. After the British research worker has spent time and trouble in making the process possible, and after technical success has been achieved abroad, the British manufacturer has just awakened to the fact that the fixation of atmospheric nitrogen is a commercial proposition. Before 1924 hardly any atmospheric nitrogen was fixed in this country, in spite of the lesson of the war. Fortunately private enterprise is taking a hand. The Imperial Chemical Industries Ltd. is now operating synthetic ammonia plants capable of producing 150,000 tons of combined nitrogen per annum. Successful atmospheric nitrogen fixation is now being accomplished in nearly every European country and in America. Before 1905 the world was mainly dependent on Chile nitrates and by-product ammonia for combined nitrogen. At the present moment Chile supplies less than 20 per cent of the world's inorganic nitrogen; by-product ammonia supplies a little more, and atmospheric nitrogen fixation processes supply about 60 per cent. Of all the countries in the world Germany is by far the largest producer. German plants are producing nearly 500,000 tons of combined nitrogen per annum.

Atmospheric nitrogen can be fixed by oxidising it at the temperature of the electric arc and absorbing the products in water to form nitric acid. This Arc process has been employed in Norway, France, Germany and Switzerland. Or calcium carbide can be heated electrically in nitrogen gas to form cyanamide or nitrolime. The Cyanamide process is largely used in France, Norway, Sweden, Germany and America. Nitrogen will also combine directly with hydrogen under certain conditions to form ammonia. This so-called Synthetic Ammonia process was extensively developed in Germany during the war. The nitrogen so fixed can be converted into nitric acid for the manufacture of explosives such as: nitroglycerin, the basis of dynamite, from nitric acid and glycerin; gun-cotton from nitric acid and cotton; T.N.T. from nitric acid and toluene; picric acid from nitric acid and phenol (carbolic acid); ammonium nitrate from nitric acid and ammonia. Calcium cyanamide on treatment with steam gives ammonia, which can be oxidised to nitric acid, or neutralised to form ammonium sulphate and phosphate. In order to compete with the natural supplies of combined nitrogen, the cost of energy used in fixation must be small and the supply of power must be on a large scale. It is for this reason that the synthetic nitrogen industry was first developed in countries with abundant water power. In this country but little water power is available, and we are consequently forced to rely on coal for the generation of the electricity needed to bring about the fixation. Splendid opportunities exist, however, for developing the nitrogen industry in Canada, Australia and other parts of the Empire, where unlimited water power can be utilised. The aggregate potential water power of the Empire is estimated to be over 50 million h.p. About 400,000 is available in Scotland alone. Little account has been taken of the "green coal," the energy of the tides, which could be harnessed to provide electrical energy. In Germany much cheap brown coal is used.

Far from being of recent German origin, the process of atmospheric nitrogen fixation is based upon fundamental facts discovered by Henry Cavendish in the eighteenth century. In 1781 he discovered that when hydrogen and air are exploded together, water and a trace of nitric acid are formed. He also showed in 1784 that atmospheric nitrogen and oxygen combine when exposed to electric sparks to give a gas that dissolves in alkalies to form nitre. For years these remained laboratory experiments until Lord Rayleigh pointed out in 1897, during his investigations on argon, that increased yields could be obtained by using a powerful electric arc to effect the combination of nitrogen and oxygen. He obtained a yield of 46 grams of nitric acid per kilowatt-hour; the most modern plant obtains 62 grams. This piece of purely "academic" research work was of the type that fails to interest the hard-headed business man, but it showed the possibilities of industrial nitrogen fixation. The important discoveries of chemical industry are made by those interested in chemistry for its own sake, and not by technical assistants working under orders in factories. In 1899 McDougall and Howles attempted to put Rayleigh's investigations on a technical basis, but their efforts and those of two Americans, Lovejoy and Bradley, were unsuccessful. Lovejoy and Bradley erected a large factory near the Niagara Falls in 1900, but after running for just over a year the work was abandoned owing to technical difficulties with the plant and to the small yield of nitrate obtained.

The first successful technical fixation of atmospheric nitrogen was achieved in 1903 by Dr. Birkeland, Professor of Physics at Christiania, and Dr. Samuel Eyde, an engineer. Their joint efforts established a flourishing nitrogen industry in Norway, although their original Arc process has been abandoned. In 1905 the now famous works at Notodden, below lake Tinnsjö, were erected with a capacity of 2,500 h.p. Subsequent enlargements in 1909 brought the capacity up to 60,000 h.p. In 1911 the company concerned, the Norwegian Hydro-Electric Nitrogen Company (Norsk Hydro), built another factory at Rjukan with a capacity of 130,000 h.p., which was increased to 260,000 h.p. in 1915. To ensure a constant water supply a dam was constructed so that a reservoir with a capacity of 190,000,000,000 gallons was formed. At present some 540,000 h.p. is expended in Norway on nitrogen fixation. With her abundant hydro-electric power Norway can produce synthetic nitrates at less cost than the naturally occurring Chile nitrates.

When nitrogen combines with oxygen heat is absorbed—we say that the reaction is *endothermic*—and heat must be continually applied for combination to continue. But the reaction between oxygen and nitrogen, resulting in the formation of nitric oxide, NO, is a reversible one.

$$\underset{\text{nitrogen}}{N_2} \quad + \quad \underset{\text{oxygen}}{O_2} \rightleftharpoons \underset{\text{nitric oxide}}{2NO}$$

Some of the nitric oxide formed is decomposed, and at a given temperature a state of equilibrium is reached. The chemist knows that a reaction occurring with absorption of heat ($N_2+O_2 \longrightarrow 2NO$) is favoured by a rise in temperature. From this we should expect that the yield of nitric oxide will increase with rise of temperature. This is found to be so, and to obtain the maximum yield the temperature should be as high as possible, as the following figures show:

TEMPERATURE	PERCENTAGE OF NITRIC OXIDE
2400 °C	2
2560 °C	3
3100 °C	5·2
3300 °C	6

Moreover the combination of nitrogen and oxygen is more rapid at higher temperatures. As the nitric oxide cools down

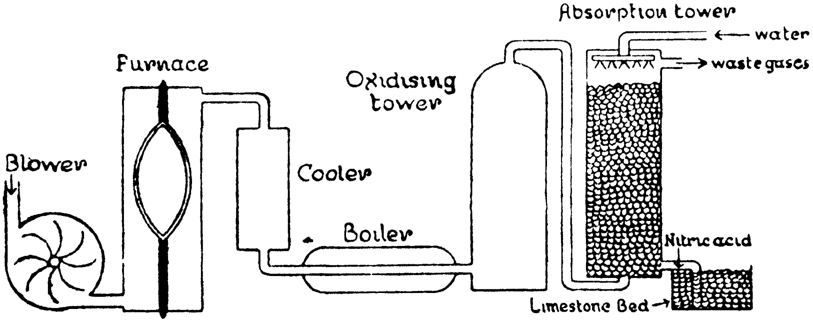

Absorption tower
water
waste gases
Furnace
Oxidising tower
Blower
Cooler
Boiler
Nitric acid
Limestone Bed

Diagram of Arc Process for preparing nitric acid from the atmosphere.

[From Partington's *Everyday Chemistry*.

FIG. 30

it will decompose into its constituent elements, but if it is cooled very rapidly the rate of decomposition is very slow, and at temperatures in the region of 800° C. to 1,000° C. it is almost negligible.

These principles were observed in the now obsolete Birkeland-Eyde process. Air was blown into a special furnace enclosing an electric arc, which was spread out into a circular sheet of flame by powerful electro-magnets (Fig. 30). At the high temperature in the region of the arc (3,000° C.) atmospheric oxygen and nitrogen combined to form nitric oxide, and this diluted with much air passed into a large iron tube lined with firebricks, in which the temperature of the gases dropped to 1,000° C. The temperature was further reduced by passing through steam boilers, and finally through water-cooled pipes, the rapid cooling preventing the decomposition of the nitric oxide. The gases then passed into a vertical iron tower lined with acid proof stone, in which the nitric oxide was oxidised to nitrogen peroxide, NO_2, by the oxygen of the air.

$$\underset{\text{nitric oxide}}{2NO} + \underset{\text{oxygen}}{O_2} \rightleftharpoons \underset{\text{nitrogen peroxide}}{2NO_2}$$

The gases were finally passed into large granite absorption towers, 65 feet high and 20 feet wide, in which the peroxide was converted into dilute nitric acid by the combined action of air and water. The dilute acid was either worked up into concentrated acid or converted into calcium nitrate, or Norwegian saltpetre, by treatment with limestone.

In spite of the success of this process—38,000 tons of nitrogen were fixed in Norway in 1927 by means of it—it has given way to a cheaper one. The power consumption of the Birkeland-Eyde process was so high that it has been found more profitable to convert the atmospheric nitrogen into ammonia, by combining it with hydrogen, and then into nitric acid by burning the ammonia under suitable conditions. Instead of being used to generate large electric arcs, the hydro-electric power of the Norwegian chemical plant is now used for the electrolytic production of hydrogen, from which ammonia is made.

The nitric acid plant devised by Schönherr and Pauling depends upon the same principle as the Birkeland-Eyde process, although they are entirely different in construction. In the former, the electric arc is produced in a vertical tube about 20 to 30 feet long through which air is forced in a spiral manner, alternately striking the arc and the cool walls of the steel tube in which the arc is maintained (Fig. 32). Since the arc is spread by the passage of the air itself, consequently no energy is required for electro-magnets to spread the arc as in the Birkeland-Eyde process; this effects a considerable saving. Some Schönherr furnaces are in use in Norway and at the Badische-Anilin und Soda-Fabrik factory, Ludwigschafen, Germany. In the Pauling process, which is operated in France, Austria and Italy, an arc is struck between two water-cooled horn-shaped electrodes of an aluminium alloy (Fig. 31). A pre-heated current of air is then blown between the electrodes, and it blows the arc upward until it breaks and a new arc forms. The air thus passes through a rapid succession of arcs. The gases leaving the arc in both the Schönherr and Pauling processes are worked up for nitric

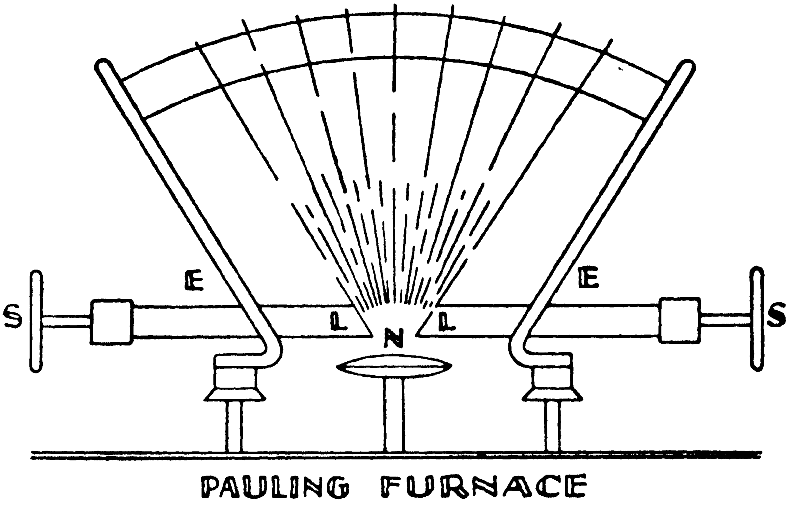


FIG. 31

A stream of pre-heated air passes from the nozzle N between the horn-shaped electrodes, EE. "Lighting knives", LL, at the base of the electrodes can be brought close to one another by the screws SS and serve for the passage of an electric arc. As the air is blown through the latter a V-shaped flame is formed. The oxides of nitrogen produced at the high-temperature are swept away in the air current and absorbed either by water to form nitric acid or by alkali to form nitrates.

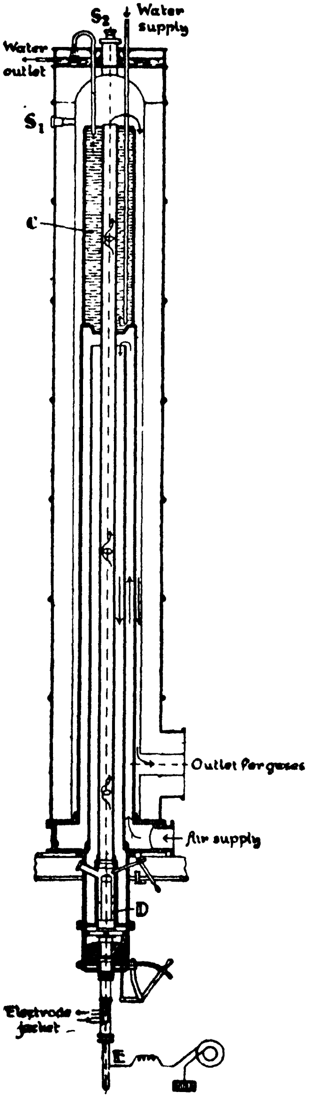

S_2
Water supply
Water outlet
S_1
C
Outlet for gases
Air supply
D
Electrode jacket
E

DIAGRAM of SCHÖNHERR FURNACE

FIG. 32

The electric arc is started by moving the iron rod L towards the insulated electrode E. Air enters at the bottom of the furnace and passes into the combustion chamber, in which the electric arc is operated, through several rows of tangentially bored holes. The air current is regulated by the damper (D) and passes through the arc with a rotating movement, shown in the diagram by curly arrows. The hot nitrous gases formed by the combination of atmospheric nitrogen and oxygen pass the water coolers (C) into the exit main and so to the plant for absorption to form nitric acid or nitrates. S_1 and S_2 are sight holes for observing the interior of the furnace when working.

acid and nitrates as previouly described. The Pauling furnaces are much smaller than those of the Birkeland-Eyde or Schönherr type, and are specially suitable for small works where power can only be utilised intermittently. There are indications that the Schönherr and Pauling processes will go the way of the Birkeland-Eyde process. In all arc methods the power consumption per given weight of nitric acid is high, and the absorption towers for the nitrogen peroxide are very costly. Before the war much German capital was invested in arc plants, but in 1913 these were sold to Norway, and Germany turned her attention to the synthesis of ammonia, in which the energy consumption is low. With the electric power requirements for the fixation of one ton of nitrogen by the arc process, four tons can be fixed by the synthetic ammonia process, and in addition the plant cost per annual ton of nitrogen in the latter is less than half that of the arc process.

The important process for the synthesis of ammonia from the nitrogen of the air, which depends upon the direct combination of nitrogen and hydrogen, is known as the Haber process, since the first successful commercial synthesis was achieved by Haber, the German chemist. In the early part of the century it was realised that the methods of nitrogen fixation in use depended upon the employment of cheap electric power, and researches were instituted in Germany—a country poorly provided with water power—with the idea of devising a method of nitrogen fixation with a minimum power consumption. Although many experimenters had studied the problem of ammonia synthesis since 1839, when Kuhlmann combined nitrogen and hydrogen by submitting them to the action of electric sparks, no commercial success was achieved until Haber and Le Rossignol investigated the process, and showed that the combination of nitrogen and hydrogen could be effected by subjecting them to high pressures. Haber's process was first proposed in 1905, when large scale experiments were made at Karlsruhe University. The high pressures demanded by Haber's method met with the disapproval of manufacturing firms, who at first considered the process impossible. Haber, however, constructed his apparatus in his own workshop and soon convinced the manufacturers of the commercial value of his discoveries. In 1910 his process was taken up by the great Badische firm (now part of the I. G. Farben-Industrie A. G.), and in 1913 a large factory was built to Haber's designs at Oppau, near Ludwigshafen. The process was so successful that when war broke out in 1914 Germany was completely independent of combined nitrogen. Throughout the war Haber's details were kept secret, and the process was brought to a very high degree of perfection by continual research. There is no doubt that Germany's colossal output of combined nitrogen for explosives came from the Haber factories. The ammonia output of the Oppau and Merseburg factories increased from 25 tons per day in 1914 to 650 tons in 1918. During the war Germany used 200,000 tons of nitric acid a year for explosives. The present total annual capacity of Haber ammonia plant in Germany is equivalent to 402,500 tons of combined nitrogen. It is noteworthy that most of the pioneer workers in this field of activity were "academic" chemists, who had no idea of the commercial applications of their researches when these were commenced. Most important commercial discoveries are made, not by technical chemists at all, but by the so-called academic chemists who are not primarily concerned with the commercial exploitation of the results of their research. In 1919 Haber was awarded the Nobel Prize for his work.

A mixture of nitrogen and hydrogen can be kept for years without any ammonia forming. If, however, we subject the mixture to the action of electric sparks very minute amounts of ammonia are formed. On the other hand when electric sparks are passed through ammonia, nitrogen and hydrogen are produced. The action is evidently a reversible one, and any attempt to effect the combination of nitrogen and hydrogen results in an equilibrium:

$$N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$$

1 molecule of nitrogen 3 molecules of hydrogen 2 molecules of ammonia

Nernst and Haber found that appreciable quantities of ammonia were formed when nitrogen and hydrogen were heated under high pressures (e.g. 200–500 atmospheres, or 3,000–7,500 lbs.

per square inch), but the *rate* at which the reaction occurred was so slow that it precluded any possible commercial application of the process. Now the chemist is familiar with many substances, termed catalysts, that possess the power of speeding up the rate of sluggish chemical reactions. We may compare their action to that of oil on machinery, or we may further compare them to a good "mixer" in society; they bring about an intimate union of substances that normally show little tendency to react with one another. Haber found that the rare metals osmium and ruthenium accelerated or speeded up the rate of reaction between hydrogen and nitrogen. Since these metals were too costly for the technical process, Haber searched for cheaper catalysts, and he discovered that the metal uranium and finely divided metallic iron containing a trace of molybdenum were very effective. It has also been noted that the addition of traces of substances that have no catalytic effect by themselves increase the activity of a catalyst used in a particular reaction. These substances are termed *promoters*. Thus the oxides of iron, aluminium and magnesium increase the activity and prolong the life of the catalysts used in the ammonia synthesis. Pure iron itself has little catalytic action, but with small amounts of a promoter it is one of the best catalysts known. The catalyst used in America during the war consisted of pumice impregnated with a mixture of finely divided nickel and a compound derived from sodium and ammonia, termed sodamide. In this country the Synthetic Ammonia and Nitrates Ltd. claim that a calcium-iron alloy is most effective.

In the Haber process a mixture of nitrogen and hydrogen, under a pressure of 200 atmospheres (3,000 lbs. per square inch), is passed over the catalyst contained in a tubular vessel of great strength heated electrically to a temperature of 500° C. (Fig. 33). Once the reaction has started further heating is unnecessary. After leaving the reaction vessel the gases, which contain 10 per cent of ammonia, are treated with water to dissolve out the latter, and the unchanged nitrogen and hydrogen after being dried are again passed over the catalyst. The reaction vessels, or ammonia converters as they are called, are usually made of a special chromium-vanadium steel or a nickel-chromium alloy to withstand the very high pressures.

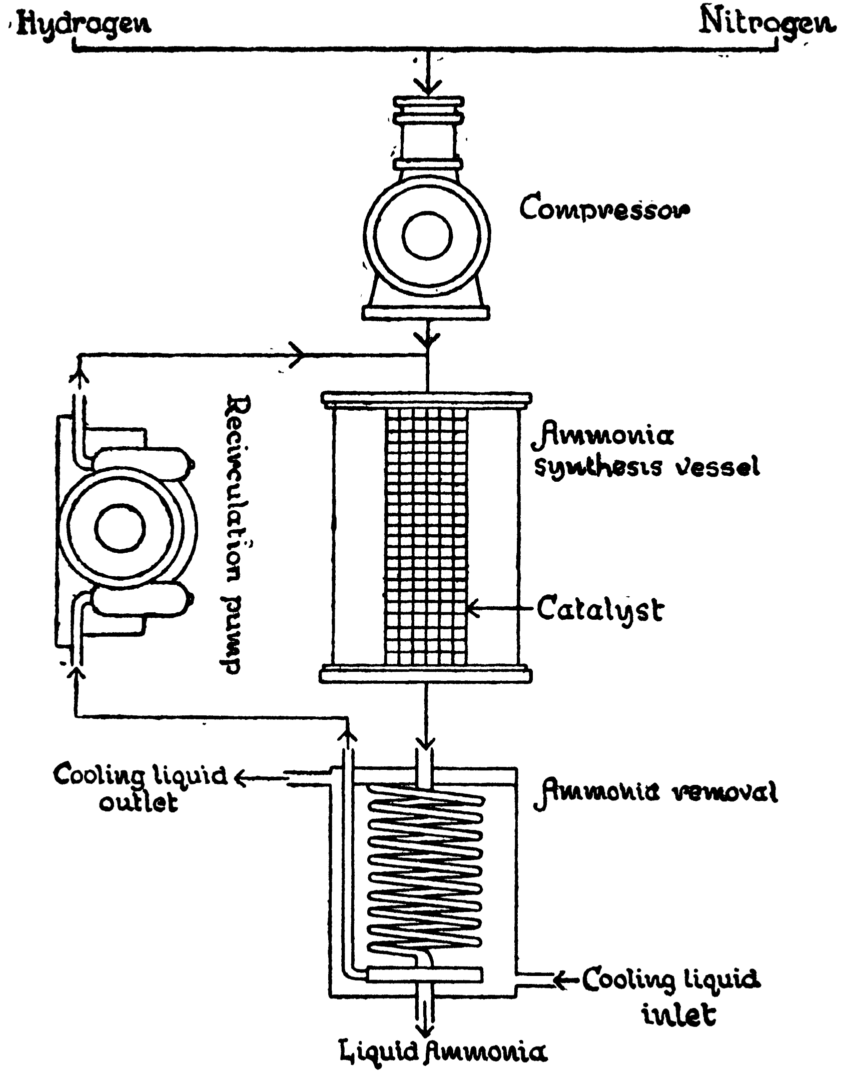

Hydrogen
Nitrogen
Compressor
Recirculation pump
Ammonia synthesis vessel
Catalyst
Cooling liquid outlet
Ammonia removal
Cooling liquid inlet
Liquid Ammonia

Diagram of apparatus for synthesis of ammonia (*Haber*)

[From Partington's *Everyday Chemistry*

FIG. 33

They are about 3½ feet in diameter by 40 feet high. The nitrogen and hydrogen required are obtained mainly from water gas and producer gas. By passing steam over red hot coke hydrogen and carbon monoxide are formed, and treatment of the mixture (water gas) with more steam in the presence of a catalyst, usually iron oxide, increases the hydrogen content from 50 to 90 per cent; this is the principle of the Bosch process (*see* Plate 24). Other sources of hydrogen are coke oven gas (55 per cent hydrogen), and the electrolytic hydrogen formed as a by-product in a number of electro-chemical processes (chlorine, caustic soda). Quantities of hydrogen are also formed in the manufacture of the solvent *butanol* (butyl alcohol, p. 317), and in America this hydrogen has been utilised for ammonia synthesis. The necessary nitrogen is obtained from producer gas, a mixture of nitrogen and carbon monoxide made by blowing air over glowing coke, and from air, which is liquefied and fractionally distilled.

Modifications of the Haber process are now being used in France and Italy. Georges Claude's process, operated in France, employs a pressure of 900—1,000 atmospheres (13,500 to 15,000 lbs. per sq. in.) and the synthesis takes place at 700° C. The percentage of ammonia formed in the Claude process is 25 per cent, as against 6 per cent obtained by the Haber process, and with this high percentage cooling with water readily liquefies the ammonia, which can thus be easily separated from unchanged nitrogen and hydrogen.

The output in the Claude process per given weight of catalyst is high, but this is balanced by the high working costs necessary to maintain greatly increased pressures. Another European development is due to an Italian engineer, Giacomo Fauser, who has perfected a modified Haber process in Italy. He uses a pressure of 250 atmospheres and a temperature of 600° C.; the yield is 4 per cent. The whole question of temperatures and pressures is a matter of compromise between output, capital charges and working expenses. Ammonia synthesis is a new world-wide industry that is sounding the death-knell of some of the older methods of nitrogen fixation. During the last year about 600,000 tons of atmospheric nitrogen were converted into ammonia.

With the fixation of nitrogen as ammonia the problem of supplying industry with fixed nitrogen is not solved. Although combined nitrogen in the form of ammonia can satisfy the demands of agriculture, the nitrogen in this form is less effective than nitrate nitrogen as a fertiliser. The difference, which is quite small, is compensated by the lower price of synthetic ammonia. Other industries, however, imperatively demand combined nitrogen in the form of nitric acid. In time of war large quantities are required for explosives, and during the last war the whole nitrogen industry was directed towards the production of fixed nitrogen in a form available for this purpose. A nation to be self-supporting in time of war, must possess means of converting synthetic ammonia into nitric acid. The conversion of ammonia into nitric acid is accomplished by oxidation, as the following reaction shows:

$$\begin{array}{ccccccc} NH_3 & + & 4O & \longrightarrow & HNO_3 & + & H_2O \\ \text{ammonia} & & \text{oxygen} & & \text{nitric acid} & & \text{water} \end{array}$$

In practice the reaction is not as simple as this. Actually the gas nitric oxide, NO, is formed first, and this combines with the oxygen of the air to form nitrogen peroxide. As we have seen, this dissolves in water in the presence of atmospheric oxygen to give nitric acid (Fig. 34). The technique of the

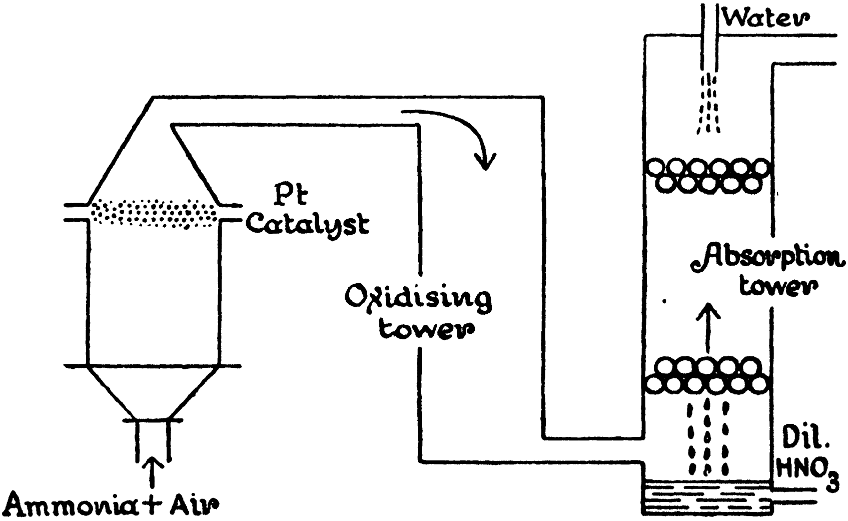


Diagram of the Ostwald process for making nitric acid by the oxidation of ammonia.

[From Partington's *Everyday Chemistry*

FIG. 34

process is largely due to the investigations of the German chemist, Ostwald, in the early years of the present century. Long before 1914 he pointed out to the German Government the necessity of developing an efficient ammonia oxidation process for preparing nitric acid in times of war. The first industrial plant operating Ostwald's process was erected at Gerthe, Westphalia, in 1908, and by 1914 five plants existed, turning out between them 260 tons of nitric acid per day. This was increased to over 700 tons in 1918. At the moment, Germany produces twice as much combined nitrogen as she needs for agriculture and industry in peace time. All the nitric acid required for explosives in Germany during the war years was obtained by first fixing atmospheric nitrogen as ammonia, and then oxidising this to nitric acid. Besides being used for the production of nitric acid, the catalytic oxidation of ammonia is being employed for the preparation of the nitric oxide that is used as a catalyst in the manufacture of sulphuric acid.

The catalyst used to bring about the oxidation of ammonia is platinum drawn out into thin wire and woven into a fine mesh gauze. Ammonia gas and air (to supply the oxygen) are rapidly passed through a converter containing the platinum gauze heated electrically to about 800° C., and although the gases only come in contact with the platinum for two thousandths of a second, yet 85 per cent of the ammonia is converted into nitric acid. Cheaper metal catalysts have been used but they are not as satisfactory as platinum. Although the preparation of nitric acid by ammonia oxidation has been condemned by military experts as a roundabout method, it enables the uncertain war-time demand for combined nitrogen to be developed from the peace-time synthetic ammonia industry. In the event of war, ammonia can be readily oxidised into nitric acid.

Another process of nitrogen fixation, which rivals the ammonia synthesis and has found successful application since 1906, was discovered by the German chemist Rothe. During some research on a new method of making cyanides for gold extraction, he discovered that strongly heated commercial calcium carbide absorbs gaseous nitrogen to form calcium cyanamide, $CaCN_2$, a nitrogen compound that can be used as a source of ammonia. Curiously enough, pure calcium carbide does not react with nitrogen. The impurities in the commercial product probably act as catalysts. Rothe's experiments had far-reaching results and ultimately led to the establishment of the great cyanamide industry. The cyanamide process essentially consists in electrically heating calcium carbide for 24 to 48 hours in drum-shaped vessels through which atmospheric nitrogen is passed under pressure. The nitrogen is obtained from liquid air. Calcium cyanamide and carbon are formed:

$$\underset{\text{calcium carbide}}{CaC_2} + \underset{\text{nitrogen}}{N_2} = \underset{\text{calcium cyanamide}}{CaCN_2} + \underset{\text{carbon}}{C}.$$

The product, which contains 20 per cent nitrogen, is known commercially as *nitrolime*, *Kalkstickstoff*, and in America as *lime nitrogen*. Its most important use was originally as a nitrogenous fertiliser; its fertilising value for cereals very nearly equals that of ammonium salts. Much of the cyanamide now produced is converted into ammonia by treatment with superheated steam in metal vessels with bolted lids called autoclaves. The cyanamide is completely converted into ammonia and calcium carbonate (chalk):

$$\underset{\text{calcium cyanamide}}{CaCN_2} + \underset{\text{water}}{3H_2O} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{ammonia}}{2NH_3}.$$

In 1906 cyanamide was first prepared technically in Italy. The industry subsequently developed rapidly in Germany, Scandinavia, Switzerland, France, Austria and Japan. The world output, which jumped from 140,000 tons in 1911 to 266,000 tons in 1913, was quadrupled during the early war years. The present output stands at 500,000 tons, of which Germany produces 200,000. Cyanide is produced by heating a mixture of cyanamide and sodium chloride in an electric furnace.

The successful development of another process for fixing nitrogen is intimately connected with the aluminium industry. The Serpek process, which has been worked in France and America, uses aluminium oxide or bauxite. Bauxite, the mineral employed in the electrolytic manufacture of aluminium, is mixed with powdered coal and the mixture electrically heated to 1,800° C. in a revolving furnace through which passes nitrogen. The aluminium nitride formed is then treated with water under pressure to produce ammonia and pure aluminium oxide, suitable for the preparation of metallic aluminium. The establishment of the Serpek process upon a sound commercial basis is only possible by reducing the temperature of operation (1,800° C.), which cannot be economically maintained for continuous periods in furnaces; the demands made on the furnace lining are too great. The proposal to install the process in connection with a 40,000 h.p. aluminium factory in Norway was abandoned in 1914.

Attempts have been made to fix nitrogen in the form of cyanides. During the war a process was devised by Professor Bucher, of Brown University, U.S.A., for obtaining sodium cyanide by heating sodium carbonate (washing soda) with coke and metallic iron in a current of nitrogen or producer gas, the iron acting as a catalyst. The U.S.A. Government investigated the Bucher process, and in 1918 built a large plant for its operation at Saltville, Virginia, but owing to high operating costs the project was abandoned shortly afterwards.

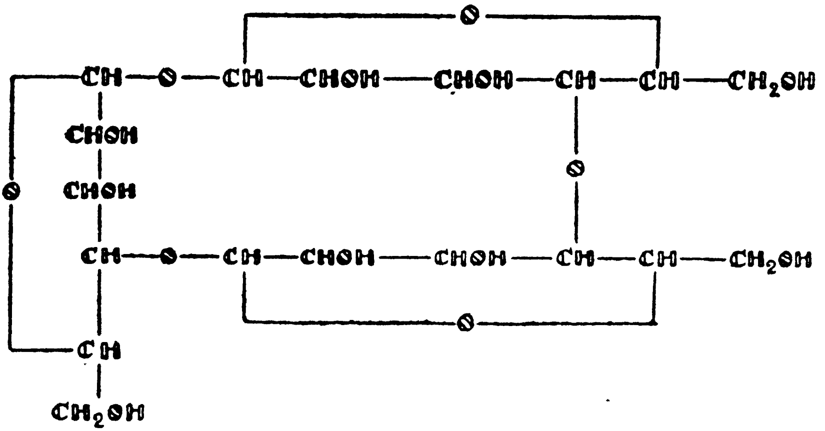
At the present moment there is no nitrogen problem in the sense that we are facing nitrogen starvation. There is now no possibility of a shortage of fixed nitrogen; the problem is how to sell it. Most countries are either self-supporting, or will be in the future, and as new processes are introduced they will compete with the older ones. The nitrogen problem of to-day is not one of shortage but of over-production. More nitrogen will be fixed than we can dispose of and a slump will occur in the nitrogen industry just as it did in the carbide industry in the 'nineties. At the time of writing there are serious repercussions in the nitrate market following the depreciation of Chile nitrate shares, caused by the large output of cheap synthetic nitrogen compounds.

CHAPTER X

CELLULOSE PRODUCTS: THE CHEMICAL SILKWORM

CELLULOSE, as we have seen (p. 152), is the chief constituent of the membranous cell walls of plants. Cotton, flax, wood-fibre and the paper of this book consist largely of cellulose and they may be converted into an almost pure variety of this substance by prolonged boiling with a solution of an alkali, such as caustic soda. Filter paper, which is very porous, and something like blotting paper, is nearly pure cellulose. Chemists are agreed that although they always talk about cellulose as an individual substance, several different celluloses do in fact exist, their difference depending upon their source. The fundamental units in the architecture of the cellulose molecule are the atoms of carbon, hydrogen and oxygen, and whatever variety of cellulose we analyse we always find that the ratio between the numbers of the atoms of these elements is 6:10:5—whence the provisional formula $C_6H_{10}O_5$. But we are not quite sure of the exact number of atoms of carbon, hydrogen and oxygen in each molecule of cellulose and so we represent it by the formula $(C_6H_{10}O_5)_x$.

Cellulose belongs to that group of compounds containing carbon, hydrogen and oxygen, in which the two latter are combined in the ratio to form water, i.e. 2 to 1; hence the name *carbohydrates* given to these compounds, which besides cellulose include the various sugars, such as cane sugar, glucose or grape sugar, fruit-sugar, and starch. A study of the X-ray spectra (p. 39) of cellulose has thrown much light upon the arrangement of the constituent atoms within its molecule. Cellulose appears to contain ultramicroscopic crystals embedded in a non-crystalline variety of the compound; to the naked eye and even under the microscope it appears to be devoid of any crystalline form. According to the evidence afforded by X-ray spectra, the cellulose obtained from wood, cotton and ramie fibre (the fibre from a plant of the nettle family) probably consists of aggregates of *four* $C_6H_{10}O_5$ molecules, $(C_6H_{10}O_5)_4$. As a result of very laborious and patient research Irvine, of St. Andrews University, believes that the way in which the constituent atoms of the molecule are arranged can be represented by the following formula:



This would correspond to a complex of *three* $C_6H_{10}O_5$ molecules. The dashes represent the manner in which the atoms are linked together; they are the valency bonds (p. 58).

When the chemist has analysed and ascertained the constitution of the compounds with which he deals his next step is to synthesise them. The chemist has synthesised sugar and many of the carbohydrates but he cannot synthesise cellulose. He has not yet learned to imitate the processes that go on in plants resulting in the formation of this compound; and yet he knows quite well how it is formed in the plant cell. The plants are centres of great synthetic activity and man is ultimately dependent upon them for his food, his clothes and the very chemicals with which he performs his syntheses on an industrial scale. Synthetic dyes, perfumes, drugs, camphor, explosives, flavours and synthetic plastics are obtained from coal-tar products. Coal-tar is obtained by the destructive distillation of coal and this has been formed by the slow carbonisation of the cellulose material present in the vegetable matter of the remote past. Modern chemistry, or rather modern organic chemistry, is a legacy of the primeval coal forests.

The tiniest green plant builds up cellulose from air and water. It has little traps or *stomata* on the under-side of its leaves and by means of these it captures the carbon dioxide of the air, and in some wonderful manner combines it with the water that it sucks up from the soil to form oxygen and probably a compound termed formaldehyde, which is converted as fast as it is formed into a sugar of the glucose type. Up to this point man has been able to copy the process, but not economically. He will never produce synthetic sugar on a large scale when he has such cheap labourers in the plant world. Having elaborated sugar, the plant couples up several molecules of it, eliminates some of the hydrogen and oxygen in the ratio to form water and so produces cellulose—

$4C_6H_{12}O_6$	$-$	$4H_2O$	$=$	$(C_6H_{10}O_5)4$
4 molecules of sugar		4 molecules of water		cellulose.

This is the stage that the wits of man cannot reproduce.

As it occurs in plants cellulose is not quite the simple body that we have depicted. It is usually associated with complex cellulose derivatives or compound celluloses as they are called. For example, in woody and jute fibre the cellulose exists in combination with *lignin* or *lignone*, a highly complex benzene derivative. In flax fibre it is combined with a substance known as *pectin*, which causes the jellying of fruit juices (e.g. in blackcurrant jelly). The cellulose of the stems and leaves of plants is associated with certain organic acids as the *adipo-* or *cuto-celluloses*. The separation of these complex bodies from the cellulose is important in the manufacture of paper and artificial silk from wood pulp.

Ours is a Cellulose Age just as much as it is a Steel Age. Cellulose is one of the most important and valuable substances of our present civilisation. Perhaps the layman does not realise the wonderful part that it has played in the diffusion of learning and in the production of cheap and healthy clothes. What we term the invention of printing was really the invention of paper. It was impossible to make books from the clay tablets of the Babylonians, or from the wax tablets of the Greeks, and although the Romans had dies for stamping their coins, they could not print on paper. The oldest kind of paper is the Egyptian papyrus, formed from the sliced stems of the papyrus plant; the writing was done with reed pens and carbon ink. But papyrus was too fragile to stand the impress of a die and parchment, or dried animal skin, and was too expensive. The diffusion of culture and learning among the masses and the interchange of ideas among the learned has only been made possible by the utilisation of cellulose in the form of paper. The textile industry tells a similar story. The ancient peoples used the crude products of plants, animals and the silk-worm for their textiles. The Egyptians used flax, the Indians cotton, the Greeks and Romans wool and the Chinese silk. Man is no longer dependent on these, although he still uses them. He has learned to convert wood pulp into artificial silk, and if need be his clothes could be made exclusively from this. Cellulose fabrics have brought about a social revolution; sensational as it may sound, cellulose has done as much for democracy as government legislation. An aristocracy is principally maintained by a distinction in dress, and this can only be maintained by law or costliness. Sumptuary laws prohibiting the wearing of fine clothes among poorer people were swept off the Statute book long ago, and until the chemist pressed cellulose into his service the clothes of the rich differed only in cost rather than in style from those of the lower and middle classes. Clothes made from artificial silk, which is essentially cellulose, are cheap and pleasing to the eye; so are the shoes made from artificial leather, another cellulose product. The result is that the factory girl can look as well dressed as a duchess, although she pays considerably less for her clothes.

Let us now examine the role that crude cellulose plays in everyday life. With the proteins it forms the basis of animal food, which is ultimately produced by plants (p. 180). They manufacture sugar and turn most of it into cellulose and a small amount into starch. Cellulose is insoluble and therefore we cannot use it as food; all foods must be either soluble in water or in the stomach fluids. The bran, wood-pulp and straw that were supposed to be used in the German war bread may have filled a gap in a hungry stomach, but this organ cannot digest cellulose, even under war-time conditions. Economically speaking, it would be to our advantage if we could digest cellulose; we could eat wood-pulp and boiled-up wood-waste instead of the more expensive bread. Although human beings cannot derive any nourishment directly from cellulose, the hoofed animals, upon whom we rely for a considerable part of our food, possess a mechanism for its digestion. The millions of cellulose digesting bacteria that flourish in the intestines of these animals convert the cellulose of grass and hay into a form that can be assimilated, and subsequently many of the animals are slaughtered for human consumption. There may not be much nourishment as such in sawdust, wood-pulp or any other crude form of cellulose, but when these substances are boiled up with dilute sulphuric acid they are transformed into glucose, a highly nutritious sugar; all our starchy foods are first converted into glucose by the stomach ferments before they are digested. From glucose, alcohol can be produced by fermenting it with yeast. By this means wood-waste can be converted into alcohol, and this process may be important in the future for the production of power alcohol.

The formation of coal and the decay of wood and cellulose are undoubtedly associated with the activity of certain bacteria. They live upon cellulose just as we live on food; it is their source of energy. Some bacteria digest or ferment the cellulose present in sewage and marshland—where it has been formed by the death and decay of plants—with the production of combustible gases, such as marsh gas or methane (p. 156), and hydrogen. Now the industrial chemist is not going to employ labour if he can get micro-organisms to do the work for him for nothing. Plants and micro-organisms are excellent workers; feed them well and keep them warm and they will work. The industrial control of bacterial processes is one of the conquests of the modern chemist. By the united efforts of billions upon billions of bacteria, waste-wood and other cellulose products are converted into power gas, alcohol and acetic acid for industrial purposes. Other bacteria have been conscripted to produce artificial farmyard manure from garden refuse to which nitrogenous matter has been added.

Crude or raw cellulose plays an important part in the textile industries. Cotton, flax, hemp and ramie form the basis of the finer textiles used for clothing, dress materials and decorative purposes. The coarser textiles employed for wrapping, twine and rope are made from the coarser forms of the above and also from jute, manilla and phormium, or New Zealand flax. Cereal straws supply raffia for hat making; coconut husk gives us fibre for mat making and upholstery stuffing; kapok, the fibre of a plant grown in Java, the Malay States and Ceylon, is also used for upholstery work and filling cushions.

We must not omit the constructional uses of cellulose in the form of wood for building purposes and for furniture. In the form of cork, in which the cellulose is combined as cuto- or adipo-cellulose, it enters into the composition of linoleum. This is made by applying a mixture of cork dust, mineral pigments, and oxidised linseed oil to canvas.

Paper is made from the compound or mixed celluloses occurring in vegetable fibres. In the earlier part of the last century before the days of cheap newspapers, cheap boots, compulsory education, typewriters and big business, paper was manufactured exclusively from the cellulose of cotton and linen rags. Cotton represents the purest form of cellulose known. Since the demand for paper rapidly exceeded the available supplies of these materials, man began to use wood, straw, bamboo and various grasses (e.g. esparto) as a source of cellulose for his paper. Most of these materials contain cellulose combined with lignin (ligno-cellulose) and resinous matter, and since these are worse than useless in the making of good paper, the ligno-cellulose is broken up and the lignin dissolved out by certain reagents, leaving pure cellulose which is made into paper. The logs of wood are cut into chips and boiled or "cooked" under pressure with caustic soda solution, or more usually in the case of cheaper paper with a solution of calcium bisulphite (formed by the action of sulphur dioxide on limestone or calcium carbonate). A mixture of sodium sulphate and sodium sulphide is also being increasingly employed for this part of the process and the product, known as "sulphate pulp", is largely used in America and Scandinavia for manufacturing stout wrapping paper or kraft paper. The cellulose proper is not attacked by these reagents, and remains behind in the form of a pulp, which in the case of the sulphate process is partly bleached. The cellulose pulp is washed and beaten up with water to break down the fibres into small shreds; this is wood-pulp. Pulp is also produced by the mechanical disintegration of wood by grinding it to powder against wet grindstones. Such pulp does not hold together and cannot be used alone for paper making; it must be incorporated with other fibrous material.

Valuable by-products are now obtained from the waste liquors of the pulping process. Acetone and methyl alcohol, two important industrial solvents, can be obtained by distilling the residues obtained by evaporating the liquors, or these may be fermented with a special kind of yeast to yield alcohol.

The pulped cellulose fibres obtained from the disintegrated wood, grass or rags are then bleached with sodium hypochlorite (p. 107) or bleaching powder, thoroughly washed, and passed over bands of wire gauze from which the water drains. The fibres are felted together by a vibratory motion of the gauze and passed through heated rollers to form paper. (Plate 30.) In this state the paper is porous and if intended for writing purposes or for high grade printing paper it must be sized with rosin, soap and alum. On hot-rolling, this mixture forms a glossy aluminium resinate. In addition, gypsum and china clay are often added as "fillers" or "loaders" to give the paper body and fill up the pores. A smooth surface is often produced by casein, a milk product (p. 321).

The best paper is the old-fashioned variety made from linen rags. Wood pulp paper is very inferior. Newspapers, cheap novels and magazines, which are made from it rapidly become brown and brittle and crumble to powder after some years. Posterity will certainly be fortunate in escaping from our lighter forms of literature.

Paper is not only used for printing. Plates, cups and even forks are made from it, and during the war a shortage of wool and cotton in Central Europe necessitated the manufacture of paper clothes.

An exhibit at the International Exhibition held in Paris in 1889 surprised the whole of the textile world; it was labelled artificial silk. But it was not silk, nor was it artificial. It consisted of fine threads of cellulose with a sheen very much like that of silk. Silk, the reader may be reminded, does not resemble cellulose chemically. True silk in the natural state consists of a double fibre of a substance called *fibroin*, a protein, stuck together to form a single thread by a gummy substance called *sericin*. When raw silk is boiled with soap, the sericin dissolves and the two fibroin threads separate. The name artificial silk is not altogether a good one—it should be called imitation silk. The Germans have a much better word, namely *Glanzstoff*, literally *shiny stuff*. Unfortunately the term artificial, or even synthetic, is apt to arouse a sense of prejudice among the general public. There is undoubtedly a feeling, bordering on the hostile, against the products of the chemist's art, although there is nothing artificial about a synthetic commodity. If a synthetic article looks like the natural thing, lasts as well and has more or less the same properties it is just as good. Refusal to accept it as such is a form of extreme conservatism. In many cases the synthetic products are physically and chemically identical with the natural ones. In some cases they are even better.

The inventor and manufacturer of silk is the little greenish-white caterpillar, *Bombyx mori*. By a process which still baffles every chemist it spins 500 yards of fine silk around itself to form a cocoon. History tells us that the Chinese Empress Lui-Tsu (2600 B.C.) and her husband, Hwang-Ti, made the first garments of silk. A knowledge of this wonderful substance spread from the East to the West through Greece. The Romans brought silk goods to England but when they left the only fabrics for a thousand years were of wool, linen and leather. The silk age began in England, in 1553 when Sir Thomas Gresham presented King Edward VI with a pair of Spanish silk stockings. Unfortunately the delicate young king never lived to wear them out. In the latter part of the next century the English silk trade became very prosperous on account of the religious persecution of the French Huguenots who fled to England, bringing with them their silk-worms and looms. The silk trade, however, has never assumed very large proportions because there are not enough silk-worms to supply the silk for a large population. There never could be unless everyone bred them. But every woman likes the feel of silk and it became evident that some other way must be found to make silk or something like it.

The idea of imitating the fine smooth thread of the silk-worm first suggested itself to Robert Hooke (1635–1703) who wrote in his *Micrographia* (1665):

> There might be a way found out to make an artificial glutinous composition much resembling, if not full as good—nay, better, than that excrement or whatever other substance it be, out of which the silk-worm wire-draws his clew.

Hooke further described the preparation of fine fabrics from dyed isinglass thread. In 1740 a Frenchman named Bon made stockings from cobwebs, but spiders are even scarcer than silk-worms. Shortly afterwards, in 1754, Réamur (1683–1757) revived Hooke's idea and proposed solutions of gum as a raw material. He wrote:

> Silk is only a liquid gum which has been dried. Could we not make silk ourselves with gums and resins?

At this time dresses were made in Italy from a kind of glass silk made by pulling out molten glass into fine filaments with a pointed steel rod. Dresses of this material were worn as a novelty at the Paris opera.

The next step was taken in 1844 by John Mercer, a Lancashire calico printer, who investigated the effect of alkalies on cotton cloth. In one of his experiments he filtered a 30 per cent caustic soda solution through bleached cotton and found that the latter was converted into a lustrous silk-like fabric that dyed more readily than cotton. The product obtained by treating cotton with caustic soda solution is now known as *mercerised cotton*. Natural cotton fibre is flat, like a ribbon; fibres of silk and of mercerised cotton are cylindrical and reflect light more easily, hence they appear lustrous. Cotton fibres shrink on mercerisation and in 1899, forty-five years after Mercer's discovery, H. A. Lowe showed that if the cotton fibres are stretched during their immersion in the caustic soda solution, so that they cannot shrink on drying, they are changed into smooth-walled fibres like silk.

Mercer did not make filaments of artificial silk. It was only after the discovery of nitrocellulose and its properties that attempts were made to produce commercially threads approaching natural silk in appearance. Silk waste, casein, gelatin, agar-agar and carragheen were all tried as the basis of such threads, but without success. Cellulose is the only raw material from which artificial silk has been manufactured, and in view of the enormous proportions reached by the artificial silk industry —300,000,000 pounds are produced annually—it is extremely unlikely that anything else will replace this substance, since it is available in such large quantities in the form of wood. Georges Audemars, of Lausanne, was the first to make filaments from cellulose products. In 1885 he patented a process of spinning a solution of nitrocellulose in a mixture of ether and alcohol, and he is honoured with being the first to mention artificial silk, or *soie artificielle* as he called it. Technical experience of nitrocellulose at that time, however, was so slight that Audemars' method was not commercially successful.

The artificial silk age really begins with the researches of Joseph Wilson Swan (1828–1914) and Count Hilaire de Chardonnet (1839–1924). The introduction of electricity for lighting purposes necessitated the production of fine filaments for use in electric light bulbs, and these were originally made of carbonised cellulose filaments. In 1883 Swan produced the first artificial silk by the squirting process. He passed solutions of nitrocellulose through a hole or die and projected the thread formed into water where it set. The thread was then treated to remove the nitro-groups and so destroy the explosive and highly inflammable properties of the nitrocellulose. Swan's filaments were carbonised and used in electric light bulbs.

Many of the phases of modern artificial silk filament manufacture appear to have been anticipated by Swan. He made artificial silk goods and exhibited them in London in 1885. Some of these are still in the possession of the Swan family. But the cost of Swan's artificial silk was considerably greater than the product of the silk-worm's art, and technical difficulties prohibited the commercial exploitation of his discoveries. Chardonnet adapted the experiments of Audemars and Swan to the needs of industry; he brought artificial silk from the laboratory to the public. He was a student under Pasteur at the École Polytechnique of Paris when Pasteur was investigating the silk-worm diseases that were causing such huge losses to the French silk industry. The uncertainty of the future of the natural silk industry undoubtedly inspired him to produce an effective substitute that was not dependent upon the caprice of a living organism. After some thirty years of active research he produced artificial silk on an industrial scale in 1884 by forcing collodion, that is a solution of nitrocellulose in ether and alcohol, through dies and denitrating the threads formed. Only 3 per cent of the artificial silk now made is produced by Chardonnet's method.

Although the raw material used for the new silk was the same as that employed by the silkworm, namely cellulose, it was not obtained from the mulberry tree. It is true that in his desire to imitate the silkworm, Chardonnet used mulberry leaves as a source of cellulose in his earlier experiments, but they were soon discarded and replaced by cotton and other vegetable fibres. Artificial silk is not made by spinning or twisting natural fibres together as cotton and woollen yarns are made. It is manufactured by transforming solutions of cellulose or cellulose compounds into fine filaments by chemical and mechanical means. After using pure cotton as a source of cellulose for artificial silk, it was found that the pulp of spruce trees and the fibres wrapping the cotton seed were just as effective and considerably cheaper. Perhaps the silk-worm would have done better on a diet of spruce-pulp and cotton fibre. Our ancestors first clothed themselves with cellulose in the form of leaves; then with cellulose in the form of cotton, and now the chemist, under the inspiration of woman, is turning leaves indirectly into artificial silk. Innovations in fabrics and clothing always come from woman; never from man.

For a long time the development of the industry was slow. Chardonnet's nitrocellulose process was dangerous and a general apathy towards the new silk existed among the public. The attention of inventors was accordingly attracted to the possibility of using less dangerous cellulose preparations. In 1890 a French chemist, Despaissis, showed that cellulose could be dissolved in a solution of copper oxide in ammonia, and seven years later the investigations of Pauly in Germany led to the production of artificial silk by what is known as the *cuprammonium process.* The real development of the artificial silk industry begins with Cross and Bevan's discovery of viscose in 1892 and the invention of the centrifugal spinning box by Topham in 1900. 85 per cent of the present output of artificial silk in the world is made by the viscose process. Strangely enough, when Cross and Bevan discovered viscose they were not trying to make artificial silk but better carbon filaments for electric light bulbs. Another cellulose product, cellulose acetate, was proposed by Cross and Bevan as the basis of artificial silk threads. It was not until after the war that cellulose acetate silk achieved any success. At present it has a considerable vogue under the name of *celanese.*

Let us examine the various methods by which the chemist converts raw cellulose into the closest imitation of real silk. The four different processes employed to-day are:

i. The nitrocellulose or Chardonnet process.
ii. The cuprammonium process.
iii. The viscose process.
iv. The acetate process.

They all employ cellulose derived from wood or cotton as the raw material. It might be thought that any kind of raw cellulose would serve. Experience has taught the manufacturer that the quality of the final product depends upon the quality of raw material. He only uses the best cotton linters, or the short seed hairs of the cotton seed that the spinners reject, and high grade, sulphite-bleached, spruce wood-pulp. Cotton linters form about 7 per cent of the total output of raw cotton, that is about 400,000 tons per annum are available. Of this the nitrocellulose industries consume about 70,000 tons for the manufacture of explosives, Chardonnet artificial silk, nitrocellulose lacquers, films and artificial plastics. Approximately the same amount is used for the production of artificial silk by the cuprammonium, viscose and acetate processes. The crude cotton linters (Plate 31) are purified by cleaning, crushing and pressing, and by boiling with dilute caustic soda solution from two to four hours. The product is washed free from alkali, bleached with chloride of lime, washed again, dried, pressed and cut into sheets. This form of cellulose, or α-cellulose, is insoluble in alkali. It is the best material for making artificial silk. Artificial silk made from cotton is 25 per cent stronger than that made from wood-pulp.

If wood pulp is employed, spruce wood is first barked and chipped, and treated in the same way as described under the manufacture of paper. The pulp is flattened out and cut up into sheets. Some 130,000 tons of spruce pulp are used in the viscose and cuprammonium processes. This represents less than 2 per cent of the wood-pulp output of the world; the majority of it is used for making paper. Spruce pulp is more expensive than other varieties but, with the exception of cotton, it is the only satisfactory source of cellulose. It contains about 90 per cent of α-cellulose. Two other varieties of cellulose are known, β- and γ-cellulose. The former is alkali-soluble and precipitated by acetic acid; the latter dissolves in alkalies and is not precipitated by acetic acid. In the manufacture of artificial silk there should be plenty of pure soft water available for washing the products at various stages. When a new mill is built the water is carefully analysed and softened, if need be. Hard or impure water causes the silk to be dull and lowers its value.

The stages in the preparation of the raw material can be seen from the following table:

Cotton Linters	*Spruce Pulp*
Cleaning, crushing and pressing of seed	Spruce wood
Raw linters	Barking and chipping
Treatment with caustic soda	Treatment with sulphite mixture
Washing	Washing and straining
Bleaching with chloride of lime	Bleaching
Washing and drying	Washing
Pressing and cutting into sheets	Rolling into sheets
	Drying
	Cutting

In the Chardonnet, or nitrocellulose process, the bleached cotton linters or wood-pulp are nitrated with a mixture of nitric and sulphuric acids for about two hours at from 20° C. to 48° C. until the cellulose contains from 10 to 11 per cent of nitrogen. The product, known as collodion cotton, is separated from the acids by squeezing and centrifuging and carefully washed with cold water to free it from all traces of acid. This stage of the process requires careful control, otherwise too much trinitrocellulose is formed, and this is insoluble in the mixture of alcohol and ether that is subsequently used. The excess acid is used again or sold for use in other industries, e.g. making superphosphate for manures. After nitration the cotton is broken into shreds, dried in special chambers with hot air, and kneaded with alcohol and ether in revolving cylinders for about eight hours until a syrupy liquid is formed. Then the mixture is filtered under pressure into tinned steel or copper tanks to remove insoluble matter and cellulose that has escaped nitration. The syrupy liquid is finally forced into the so-called spinning boxes from which it issues in the form of fine threads or filaments, like a spray of water from the rose of a fountain. This act of forcing the syrup through dies is called spinning, although of course it is not spinning at all in the real meaning of the word. The Germans call it *Drahtziehen* or "wire drawing", which is a much better word. Spinning is either done by the dry or the wet process; in the Chardonnet method the former is more usual. In dry spinning the syrupy mixture is forced through spinnerets or capillary glass tubes and the issuing filament wound on rotating spools. Hot air is passed over the spools to evaporate the alcohol and ether and set, or solidify, the nitrocellulose filaments. The air laden with alcohol and ether vapour is drawn through condensing towers containing activated charcoal or *silica-gel*[1] to absorb and so recover the solvents. Owing to the high cost of the latter, and to small losses in the process due to their evaporation, the Chardonnet process is rather expensive. In wet spinning—originally proposed by Chardonnet—the filament from the spinneret passes into a setting bath of water, where it solidifies. The filaments so obtained are single strands. They are twisted together on rotating vertical spindles to form threads which are reeled into skeins.

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[1] Silica-gel is made from water-glass (sodium silicate) and hydrochloric acid. It is a colloidal form of silica (silicon dioxide). There are many substances, including silica, glue, white of egg, starch, gums and gelatin, that are non-crystalline and jelly-like in appearance, and cannot pass through a membrane or filter. They are called *colloids* (from the Greek, *kolla*, glue). Any substance may be obtaned in a colloidal form under suitable conditions. The term colloid does not indicate a kind of substance so much as a *state* of matter. In a true solution the molecules of the dissolved substance are dispersed throughout the liquid. In a colloidal solution the particles of the colloid are not of molecular size; they consist of aggregates of molecules. Colloidal particles vary in size from about 10 to 10,000 times that of an average chemical molecule.

The yarn so formed is inflammable and in a mild degree explosive. It is therefore denitrated, whereby the nitro-groups attached to the cellulose are removed, leaving pure cellulose. 5 per cent solutions of ammonium sulphide or sodium hydrosulphide are employed for this purpose. Skeins of the nitrocellulose are left in the solution for about two hours and the chemicals removed by constant washing. The product is finally bleached, washed again, soaped and dried. The Chardonnet process is the most costly of all, but the artificial silk obtained has such a beautiful appearance and fetches so high a price that it can still compete successfully with the cheaper processes. There is evidence, however, that with the advent of the acetate silks it may soon disappear from the market. In 1927 only 3 per cent of the artificial silk output was made by the Chardonnet process; in 1910 it was 48 per cent.

The cuprammonium process depends upon the solubility of cellulose in an ammoniacal solution of copper oxide. Cuprammonium silk is a serious rival to the nitrocellulose silk, partly because of the heavy tax on the alcohol used in the manufacture of the latter, but mainly because of its appearance and the fineness of its fibres. It has maintained a monopoly position among the artificial silks for some time, but it cannot compete successfully with the viscose method for cheapness. The tensile strength of cuprammonium silk has, so far, not been equalled by any other product. Bleached cotton linters and bleached wood-pulp serve as a source of cellulose, although the silk from the wood-pulp has not the fine appearance and feel of the cotton product. The crude cellulose is first boiled under pressure with dilute caustic soda solution, which removes grease and at the same time dissolves all impurities, leaving α-cellulose undissolved. The mass is squeezed dry, torn into shreds, and disintegrated in a pulping engine. It is then mixed with a solution of copper sulphate, to which caustic soda has been added, and the paste formed passed through a filter press under a pressure of 200 atmospheres to extract all liquid. A mixing machine like those employed in large bakeries breaks up the paste and this is gradually stirred into strong ammonia. A little cane sugar, glucose and tartaric acid are often incorporated at this stage; they produce a fine sheen on the finished product. After filtering through a mesh of rustless steel to remove solid particles—these would choke the spinnerets—the ammonia is evaporated and air bubbles removed by vacuum. The liquid is now ready for spinning. One of the methods, based on a patent of Thiele, in Germany, is known as "stretch spinning". When the cuprammonium solution passes from the spinnerets into a setting bath of water containing a little sulphuric acid, the cellulose is thrown out of solution from the semi-liquid threads and forms solid filaments. In the stretch spinning process these are stretched while they are solidifying, or coagulating, with the result that extremely fin filaments are formed, equalling if not surpassing natural silk filaments in fineness. Traces of copper, which would affect the quality of the silk, are removed after the spinning by washing with 1 per cent hydrochloric acid. The final process consists of bleaching the threads. Thick filaments of so-called artificial horsehair can be obtained from the cuprammonium solution by forcing it through comparatively wide apertures. In order to make the cuprammonium process pay, it is necessary to recover the valuable chemicals—ammonia and copper—as completely as possible.

By far the greater part of the artificial silk of to-day is produced by the viscose process, due to two English chemists named Cross and Bevan. Nearly 250,000,000 pounds of viscose silk are made annually; this represents about 84 per cent of the world's output. The raw material used in the manufacture of viscose silk is bleached wood pulp, cotton linters, or a mixture of the two. When the pulp sheets reach the silk factory they are soaked for two hours in 17 per cent caustic soda solution, which causes the wood fibre to swell, and the excess caustic soda solution is squeezed out by hydraulic presses. The sheets of soda-cellulose formed are torn into small pieces, or crumbs, and allowed to age or mature in a closed vessel for about twenty-four hours. On no account must hard water or water containing iron be used at any stage in this process. The matured soda-cellulose is removed to an enclosed mixing cylinder, where it is agitated for three or four hours with carbon disulphide—a liquid obtained by vaporising sulphur in an electric furnace and passing the vapour over heated carbon. This results in the transformation of the cellulose into an orange-coloured, gelatinous mass called cellulose xanthate, which when mixed with water is usually known as viscose. After maturing a day or two at a low uniform temperature, the viscose becomes less viscous and fit for spinning. But before the solution is spun it is filtered and air bubbles removed by vacuum.

The viscose is now pumped to the spinning machines and spun wet. It comes out in the form of fine filaments from the spinnerets, which are immersed in a setting bath containing water, sulphuric acid and sodium sulphate. The viscose at once coagulates to form threads of regenerated cellulose, which are washed, dried, and reeled into skeins. Various deleterious by-products containing sulphur are formed in the threads during the spinning process. They are dissolved out by treating the skeins with weak sodium sulphide solution and bleaching with chlorine. An antichlor, such as sodium sulphite, is then used to remove traces of chlorine from the skeins, and these are finally washed free from chemicals, dried, washed again with a little soap to improve the feel and dried again. Many substances have been suggested and used to improve the feel and appearance of the final product. The "scroop" or rustle of real silk and its characteristic feel are imitated in artificial silk, by dipping first in a soap bath and then in another containing formic or tartaric acid. The goods are dried without rinsing. Women prefer this scroop and so it is imitated.

The appearance of the cross section of a thread of artificial silk is very important and affects the appearance of the silk when made up. A circular cross section with jagged edges like a cog-wheel or circular saw would be the best from the point of view of strength and light reflection. Such a silk would give the best colour-effects after dyeing. It has been found that the amount and nature of the substance in the setting bath affect the cross section of the threads. Apparently water containing 12 per cent sulphuric acid and from 1 to 8 per cent sodium sulphate produces the best effect. The site of a viscose silk factory is important because of the nature of the by-products —caustic soda and sulphur—which are objectionable effluents.

The world's artificial silk market has been made on viscose silk and it will probably remain the most popular, for some time at any rate, on account of its strength and the cheapness of the raw materials. Acetate silk, or celanese, is made from cellulose acetate. It has a finer sheen than viscose silk, but since it is more expensive it is not likely to displace the latter. When cellulose is treated with acetic acid, two or three hydrogen atoms are replaced by acetyl groups from the acetic acid (cf. the nitro-groups from nitric acid) and the resulting compound is known as cellulose acetate. Like nitrocellulose, it dissolves in such organic solvents as acetone and chloroform. Although the substance had been prepared in 1865 by a French chemist, Schützenberger, some thirty years elapsed before Cross, of viscose fame, patented a process for its manufacture. Cross found that acetic acid would not react readily with cellulose unless a catalyst, or chemical activator, were present and for this purpose he used zinc chloride. In the early part of the present century an American named Miles prepared a high grade variety of cellulose acetate by allowing it to ripen during its preparation. This enabled artificial silk and non-inflammable films to be made on a commercial scale. It was the war, however, that permanently established the acetate silk industry. Chemists found that cellulose acetate made an excellent non-inflammable dope for aeroplane wings, giving a shrunk finish effect, and a Government factory was erected at Spondon, Derbyshire, for the manufacture of the substance. After the war the factory was acquired by the Celanese Company and reconverted for the manufacture of acetate silk, which was subsequently known as celanese. Hosiery yarns, warp and weft yarns for weaving, and woven fabrics are now made from it.

Celanese is manufactured from bleached cotton linters, which are first treated with acetic acid, acetic anhydride (a compound that produces acetic acid with water) and a little sulphuric acid to act as a catalyst. The temperature is raised until the cellulose goes into solution, and the resulting product is then treated with water to precipitate the cellulose acetate as a white flocculent mass. It is filtered, washed free from acids, dried and dissolved in acetone, from which it is spun after being carefully filtered under pressure. The manufacturer distinguishes between "primary" and "secondary" cellulose acetate, and it is the latter, which contains more cellulose, that he uses for making artificial silk. Acetate silk is spun "dry" from the acetone solution, that is, as the semi-liquid filaments extrude from the spinnerets the solvent is allowed to evaporate, leaving a solid thread. The acetone is recovered from the acetone vapour in a special condensing apparatus, but the more expensive chemicals, acetic acid and acetic anhydride, are practically irrecoverable and this makes the process somewhat expensive. In addition, cotton costs more than the wood-pulp used in the viscose process.

It will be observed that chemically, celanese is unlike the other artificial silks, which are all forms of cellulose, or to be more exact, forms of *cellulose hydrate.* This is cellulose intimately associated with water. It is formed in the manufacture of all the artificial silks—except acetate silk—by mercerising, and by treating cellulose with strong acids and alkalies. It is also produced mechanically in the paper-makers' beater. Cellulose will absorb water and swell to a gelatinous mass in much the same way as starch—chemists call this imbibition, which simply means soaking or drinking up—and it has been proved that the water goes in *between the atoms* packed in the cellulose molecules.

In the early days of celanese it was found that it did not dye well; this was its chief drawback for use in the textile industry. Modern woman demands bright, gay colours, and a fabric that does not dye well will never achieve popularity. The difficulty of dyeing celanese was eliminated in 1920, when it was discovered that the cellulose formed by treating it with alkali, or saponifying it, dyed as well as cotton. Dyed celanese goods are now appreciated not only by many wives and daughters, but by husbands and sons. A special range of dyestuffs, known as S.R.A. dyestuffs, had to be invented for dyeing celanese. They will not dye satisfactorily the other artificial silks. By the alternate weaving of viscose and celanese, and dyeing in the same bath, two different tones or tints can be obtained in the same fabric because the two different silks have different affinities for the dye.

The other artificial silks dye like cotton. If materials made from wool, or real silk mixed with artificial silk, be dipped in a bath of two different dyes, two or three colour effects can be produced. This process, called cross-dyeing, is used for brocades. Or celanese yarn may be twisted with another yarn, and the compound yarn on dyeing will exhibit two shades of colour. Similarly it is possible to weave one kind of silk, say celanese, with another so that one forms the background and the other the pattern. After dyeing, the background and pattern differ in colour. It is possible to get eighteen different colours on one fabric.

Celanese is soft but at the same time strong, both in the wet and dry condition. All artificial silks are not so strong or elastic as the natural product, especially in the wet state, and for this reason natural silk lasts longer. It will withstand continued washing. Chemical tests show that celanese does not rot so readily as natural silk, cotton and linen, a property that makes it a suitable substance for use in the manufacture of lines and nets. It possesses a serious drawback, however, in that it does not absorb moisture readily. This property renders it unfit for underclothing, which should be able to soak up perspiration without feeling damp. Celanese is an excellent electrical insulator and is being used more and more in the electrical industry. Much of it is now being used as an insulator by the telephone department of the Post Office.

The different artificial silks have not all the same lustre. Nitro-cellulose silk is shiny; cuprammonium silk is glassy; viscose has a bright and silvery appearance; and acetate silk has a glistening metallic lustre. They can all be distinguished from natural silk by a simple test, the combustion test. Silk burns slowly, giving off a smell of burnt hair or horn and leaves a charred residue. The artificial silks burn more quickly without any smell, and leave scarcely any residue.

Great improvements have recently been made in the appearance, feel and lustre of artificial silks, especially in the viscose process. Threads can be produced as fine and nearly as strong as silk by a new process introduced in 1926 by Dr. Lilienfeld of Vienna. He employs a setting bath containing 50 per cent sulphuric acid, with the result that the filament obtained is stronger than that of any other artificial thread and approaches real silk and cotton in strength. Filaments $\frac{1}{14000}$ of an inch in diameter can be made. By making hollow fibres from viscose a product with the rustle of real silk can be obtained. This is effected by mixing the viscose with a little sodium carbonate before spinning into the acid setting bath; the bubbles of carbon dioxide formed inside the filament swell it out and thus make it hollow. The lustre of artificial silk can also be increased or decreased to suit a particular fabric, and an accurate instrument termed a glossmeter has been invented for the purpose of determining lustre. Variations in the composition and strength of the setting bath alter the shape of the filaments, upon which depends the lustre and "body" of the final fabric. Textiles of artificial silk are usually stiffened, e.g. with starch, gelatin and gum tragacanth, and loaded or weighted, like pure silk, with tin phosphate. Since silk is sold according to weight it is loaded with tin salts, which are really harmful and impair its strength. Black silk often contains four times as much loading material as silk of other colours. Loading certainly improves the look and style of silk goods and for this reason, if not for the more fraudulent one, it is likely to continue.

If handled carefully artificial silk resists the action of most chemicals used in dyeing and washing. It will stand boiling water, although it is not advisible to boil artificial silk goods; they are best washed by hand in fairly warm water with a neutral and not alkaline soap. Artificial silk absorbs large amounts of water and increases in volume up to 40 per cent, its tensile strength decreasing at the same time. This, however, is regained on drying. The taking up of water depends upon the capillary structure of the fibre and upon the large surface area of the filaments. We can change the physical nature of the silk by treating it with suitable chemicals so that it will not take up water; in other words we can waterproof it. Various waterproofing processes are known. One is based upon the treatment of the silk with formaldehyde and lactic acid. This property of absorbing moisture makes artificial silk ideal for underwear because it absorbs perspiration and allows it to evaporate slowly, thereby keeping the skin dry. Artificial silk, either alone or woven with cotton or real silk, is now used in increasing amounts for underwear. We are at last beginning to realise that we breathe through our skin—which should be kept healthy and free from evaporated perspiration—as well as through our lungs. Natural silk is also more readily rotted by perspiration than the artificial product. Further, artificial silk clothing is hygienic because it lets fifty per cent of the health-giving ultra-violet rays through; cotton, wool, linen and real silk are like armour plate to the rays. Clothes have only been worn in comparatively recent times. They brought disease, because they excluded air and sunlight, the two curative agents that are of more value than the whole of the Pharmacopœia. Savages hardly knew disease until they were wrapped up in clothes by missionaries. It is true that civilised communities cannot dispense with clothing, but they can do the next best thing—wear as little as possible, and that made from artificial silk.

In the manufacture of textiles artificial silk is often combined with natural fibres, such as silk and cotton, and attempts are being made to market it in combination with wool and linen. There is now a tubular yarn, or artificial wool, made of artificial silk under the trade name *celta*. It is warm like wool and suitable for underwear and hosiery. Plushes, velvets, rugs, curtains and upholstery are made from it. A cotton-artificial silk mixture is used for hosiery, shoe-coverings, umbrellas, cloths, ribbons and pile fabrics. Satins, laces, embroidery and draperies are made from it, and also from real silk and artificial silk mixtures. Crêpes, dress materials and brocades are also made from the latter.

Man can not only dispense with the silk-worm but with the weaver as well. Tulle and lace are made without spinning or weaving by forcing a solution of cellulose—usually the cuprammonium variety—upon a revolving metal cylinder engraved with the pattern of the desired textile. The excess cellulose is removed by a scraper and a jet of water flows over the cylinder thereby solidifying or coagulating the cellulose. This artificial lace and tulle is less pliable than that made by weaving. It has the lustre of artificial silk and may be metallised or waterproofed.

Simple as the operations that we have described may seem, they are full of complications and require the continuous attention of the most experienced chemists. Special care must be taken to see that the water supplied to the factory is soft. Precautions are needed in drying the filaments, which like furs, must not be dried too quickly, otherwise they develop stains. These often appear as a result of imperfect washing. Artificial silk factories require a special climate; they need a certain degree of humidity, just as cotton does. Again, in the viscose process the problem of maturing or ageing is important if a high grade product is desired. A knowledge of the physical and chemical properties of textiles, of the dyeing qualities of artificial silk, and of the properties of the class of substances termed *colloids*, is of great importance. Another problem that has not yet been solved concerns the tensile strength of artificial silk. It is well known that when wet it is not so strong, and hence artificial silk goods are likely to become torn during washing and laundering. The chemist has yet to produce a cellulose silk that will be as strong while in the wet condition as when dry.

Nitrocellulose, viscose and cellulose acetate besides supplying us with artificial silk, can also be worked up into a variety of other useful products. Most people have heard how Nobel, the pioneer worker on explosives and the originator of the Nobel prize, cut his finger and for want of a better styptic swabbed it with a solution of cellulose nitrate in a mixture of ether and alcohol. When the latter evaporated, a hard, elastic and waterproof skin remained, and Nobel at once realised the possibility of using such a solution for surgical work. It is now employed under the name of *collodion*. In the chapter on explosives we have seen how cellulose can take up one, two or three nitro-groups to form different nitrocelluloses. The higher nitrocelluloses, known as gun-cotton, are very explosive and insoluble in a mixture of alcohol and ether; the lower nitrocelluloses which are less nitrated, i.e. they contain fewer nitro-groups, are soluble in the mixture and form collodion. They constitute what is known as *pyroxylin* or *collodion cotton*.

Shortly after Nobel made history by cutting his finger, Hyatt, an American who started life as a type-setter, found that pyroxylin and camphor could be moulded into an extremely useful plastic material that we now call *celluloid*. In 1855 Parkes, an English inventor, made artificial plastics from pyroxylin and castor oil, but they became sticky in hot weather. Spill, an associate of Parkes, made a better product by incorporating the two substances with camphor. He called it *xylonite*. Hyatt showed, however, that camphor and pyroxylin could be incorporated without using that objectionable material, castor oil, by mixing them in alcohol as a solvent and compressing the gelatinous mass formed. Hyatt first applied his invention to the manufacture of celluloid billiard balls as a substitute for ivory ones, and some amusing stories are told concerning these. A Colorado saloon keeper wrote to Hyatt complaining that one of his patrons put down a cigarette by the side of one of the balls, which, being very inflammable, at once blazed away causing great alarm among the habitués of the saloon, who commenced firing off their guns. A humorous contemporary also suggested that Hyatt would make his billiard balls cheaper by rearing elephants.

Celluloid is manufactured to-day in much the same way as Hyatt made it in the 'seventies. Tissue paper, cotton, or cotton waste are nitrated to the pyroxylin but not to the gun-cotton stage and the product pulped, bleached, washed and dried. It is then incorporated with natural or synthetic camphor and a little alcohol in mixing machines. "Fillers" are added and, in the case of white celluloid, an antacid such as urea to prevent the finished product from turning yellow or opaque. This is caused by the gradual decomposition of the nitrocellulose and the urea neutralises the free acid formed. If coloured celluloid is desired suitable dyes or pigments can be added. The gelatinous mass is compressed into cakes, dried and pressed into the required shape in steam-heated moulds. Celluloid becomes plastic at the temperature of boiling water. Recent improvements have been made in its manufacture by precipitating it from alcoholic solution with water and filling the dried precipitate into heated moulds in which it can be fashioned into any shape.

Celluloid has many disadvantages. It smells of camphor, dissolves in hot acids and alkalies, softens when heated and, worst of all, is highly inflammable when made by the process just described. Most celluloid is now made non-inflammable, or at any rate its inflammability is considerably reduced, by the addition of tin chloride. Non-inflammable celluloid can also be made from viscose and cellulose acetate. Since camphor is rather expensive, many substitutes have been proposed. Most of these are unsatisfactory, although one of them, termed phenyl phosphate (a benzene derivative), reduces considerably the inflammability of the final product. Ivory, horn, tortoiseshell, amber, agate and marble can be imitated in celluloid, which is also used for knife-handles, collars, accumulator cases, buttons, toilet goods, transparent screens, piano keys, dental plates, photographic films, eye-glass frames, telephone mouth pieces and for many other practical and ornamental purposes. *Oralite* and *hecolite* are forms of celluloid used in place of vulcanite for dental plates. The irregular colour effects produced in imitation tortoiseshell and many fancy goods are obtained by dropping small quantities of different pigments upon sheet celluloid before heating and moulding.

The non-inflammable plastics, which are clearly more useful than celluloid, have undergone a remarkable development within recent years. A new and important group are the so-called "condensation products". In 1872 von Baeyer, the German chemist who made synthetic indigo possible, discovered that phenol or carbolic acid reacts with formaldehyde to form a gummy resinous mass. For forty years Baeyer's work remained in the archives of research and attracted little attention until Baekeland, a professor at Bruges, realised the commercial possibilities of the product. This Belgium chemist showed that if the reaction is conducted in the presence of ammonia, a resinous precipitate separates, and that if this is heated under pressure it forms a plastic material superior to celluloid. Chemists call this substance polymerised hydroxyphenylmethyleneglycol, but to everybody else it is *bakelite*. It is odourless, insoluble (except in alkalies), infusible, inert, non-inflammable and an excellent electrical insulator. Hence it is extensively used as an insulator in wireless and electrical work and as a substitute for amber. It is also used for making billiard balls, buttons, knife handles, and many other materials hitherto made from bone or celluloid and vulcanised rubber. Wood impregnated with resinous bakelite and heated gives a hard surface that polishes like Japanese lacquer. Paper, cardboard, metal articles, wood-pulp, cloth, and asbestos may be similarly impregnated. Unfortunately, bakelite can only be obtained in colours ranging from clear amber to brown and black. Instead of phenol other coal tar products such as cresol and naphthol (hydroxynaphthalene) may be used. Redman used phenol and a compound of formaldehyde and ammonia called hexamethylenetetramine. The product, which is similar to bakelite, has been named redmanol.

Another celluloid substitute, *cellon,* has been made from cellulose acetate and camphor, and in many respects is an improvement on celluloid. It is used for making non-inflammable cinema films, hairbrush bristles, imitation horse-hair for upholstery and clothing, and in solution form as a varnish for aeroplane wings, wood, paper, metal, and for electrical insulation. Another plastic body for moulded articles containing cellulose acetate is known as *lonarite.* In fact all the spinning solutions used in the manufacture of artificial silk can be converted into sheets, films, and moulded articles. Since cellulose acetate transmits ultra-violet light better than glass it is used for transparent screens, motor goggles and unbreakable "glass" windows. Safety glass is a three-ply material made by cementing nitrocellulose or cellulose acetate films between two thin sheets of glass.

When viscose is kept for some days it forms a hard horny material known as *cellophane.* Thin transparent films of this substance can be made by spreading warm viscose on glass. Sheets of cellophane are used for wrapping foods, cigarettes, chocolates and as a coloured sealing cap for chemists' bottles.

If nitrocellulose is mixed with a drying oil, such as linseed oil, and spread on cloth it forms an effective imitation leather that can be coloured and grained. It is used for furniture and car upholstery under the name *rexine* and *pegamoid.* Fortunately imitation leather has arrived at a period when pasture land is getting scarce. Most cheap " leather " goods, including footwear, are cellulose products.

Hard films, suitable for use as parchment, for decorative purposes, fine boarding, bookbinding, and in the manufacture of artificial flowers, can be produced from the cellulose solutions. Waterproofed fabrics are also made by passing ordinary fabrics through cuprammonium cellulose solutions. *Willesden* goods are prepared in this way. Parchment paper, or "vegetable parchment", is obtained by passing sheets of paper through cold, slightly diluted sulphuric acid, or zinc chloride solution and then washing. Both chemicals act upon the cellulose of the paper, converting it into a jelly that fills up the pores. Similarly, cotton fabrics can be treated quickly with sulphuric acid to produce what are known as "transparent textiles" with a moiré effect. The sulphuric acid dissolves the outer surface of the cotton fibres and changes these parts to a jelly-like mass that gives a brilliant silky effect. If left in contact with the acid for some time the fabrics would, of course, rapidly rot. Paper, "vulcanised" by being passed through a 30 per cent solution of zinc chloride, forms a hard fibrous mass when subjected to pressure. This compressed or so-called vulcanised fibre is largely employed in making cheap trunks and cases, and as an insulator for electrical purposes.

During the last decade nitrocellulose has been widely employed in the manufacture of cellulose lacquers and enamels, which are used for decorative work and for imparting the "cellulose finish" to motor-car bodies. A cellulose lacquer consists essentially of nitrocellulose dissolved in suitable solvents with a pigment, or not as the case may be. Since nitrocellulose films themselves do not adhere readily to wood or metal, gums and plasticisers are incorporated in the lacquer to prevent too rapid drying and to confer plasticity. A few years ago acetone and amyl acetate, the ester[1] with the smell of pears, were almost the only solvents available. During the war the large demand for acetone led to its manufacture from grain and potatoes by a fermentation process, which produced considerable quantities of butyl alcohol as well. Butyl acetate, a compound of butyl alcohol and acetic acid, is now used as a solvent. Ethyl lactate, cyclohexanol—produced by hydrogenating phenol under high pressure in presence of a catalyst—and a liquid known as cellosolve are also employed. Many liquids, not in themselves solvents for nitrocellulose, form good solvents, when mixed with each other in the right proportions, e.g. benzol and ordinary alcohol. Only sufficient solvent is needed to keep the nitrocellulose in solution. More liquid, termed a diluent, is added however to thin down the solution and make it workable. The chief diluents are light petroleum spirit and other petroleum and coal-tar products. Gums, both natural and synthetic, are introduced into the lacquers to make the nitrocellulose film adhere and prevent peeling. Kauri, copal and benzoin gums are used for the purpose. A synthetic resin employed in America is obtained by the action of sulphuric acid on cumarone and indene, two constituents of the high boiling fractions of coal-tar naphtha. Other synthetic resins are prepared in a similar manner to bakelite; that is by "condensing" formaldehyde with phenols. The function of the plasticiser is to eliminate the brittleness of the nitrocellulose film, toughen it, and render it flexible without unduly softening it. Many manufacturers are still using that nursery medicine, castor oil, and camphor as plasticisers, but the greatest success has been met with some complicated chemicals which, whilst acting as plasticisers, are also solvents for nitrocellulose. Diethyl phthallate and tricresyl phosphate belong to this class. The former is obtained by the action of ordinary alcohol on an oxidation product of naphthalene. Tricresyl phosphate is formed from phosphoric acid and cresol, which accompanies phenol in coal-tar.

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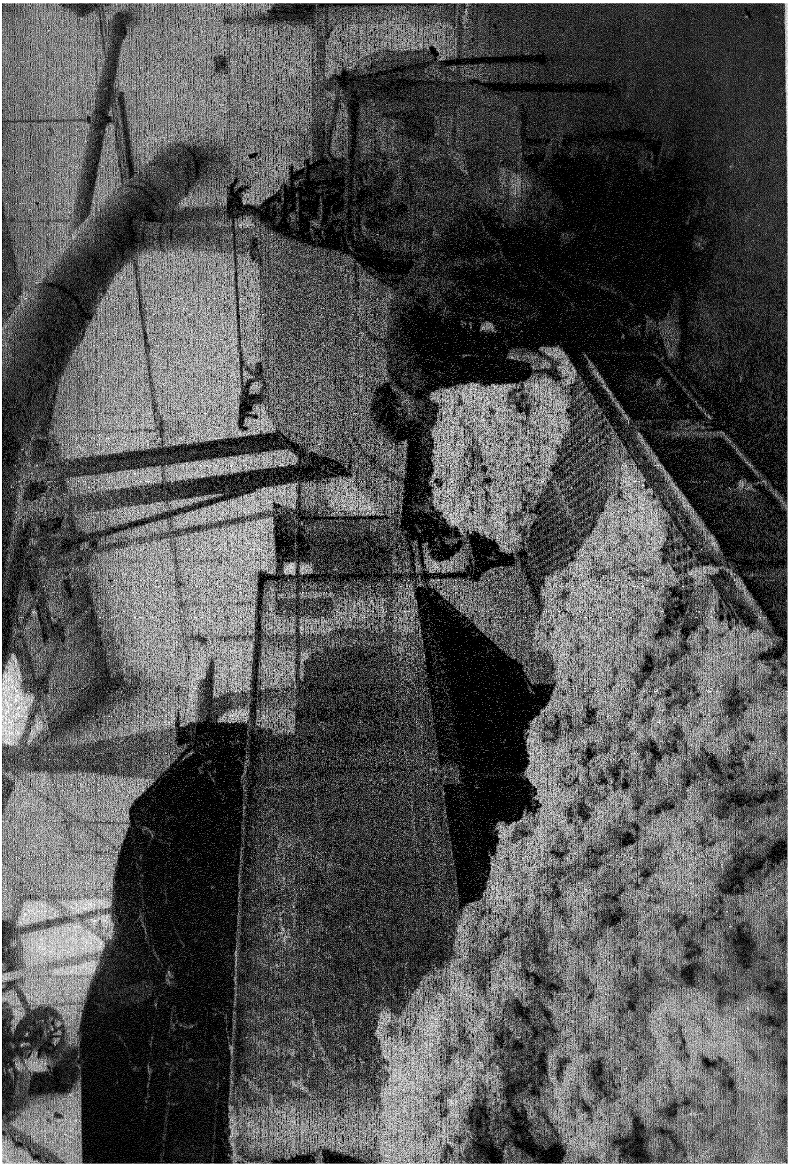
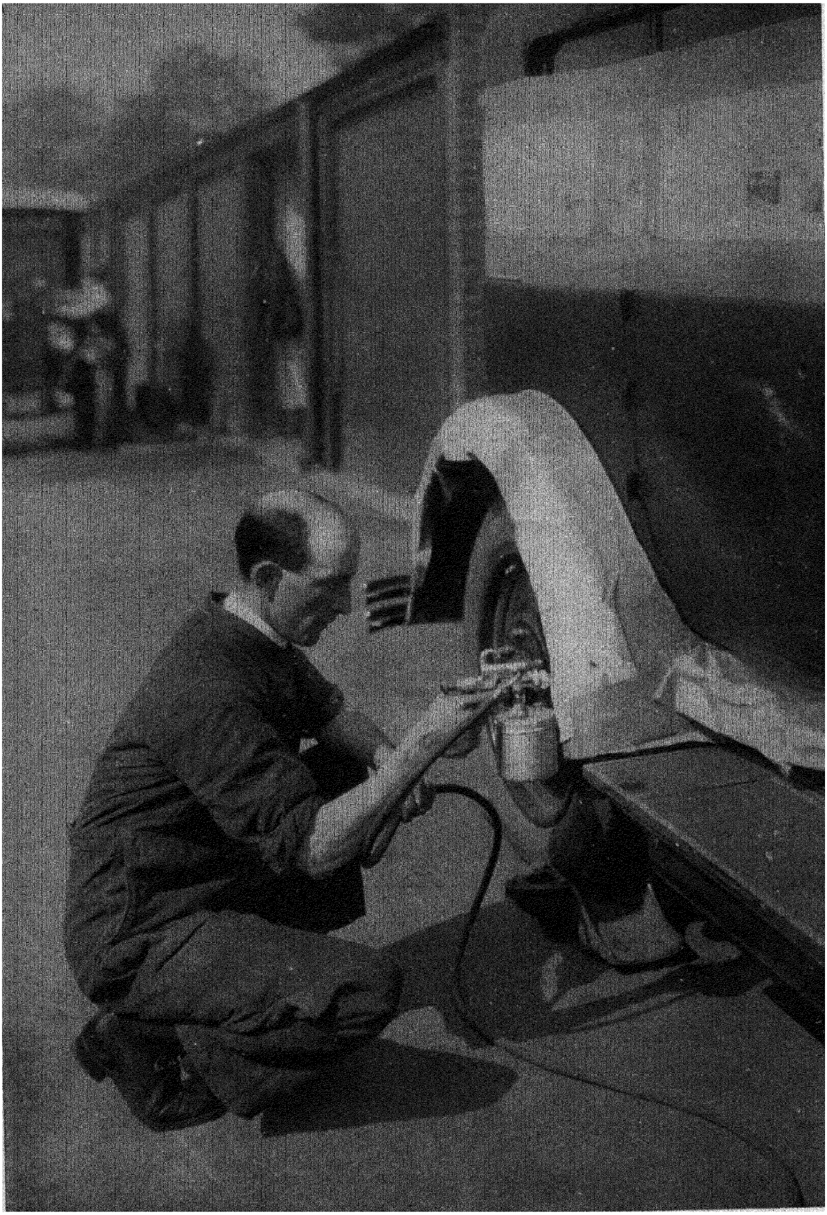
[1] Esters are compounds formed by the action of acids on alcohols. Thus ethyl alcohol (ordinary alcohol) forms ethyl acetate with acetic acid; amyl alcohol forms amyl acetate; butyl alcohol forms butyl acetate; and so on.

Cellulose lacquers resist the action of acids, petrol, water and to some extent the abrasive action of mud and dust. They can be applied to wood, metal and glass. Recent applications are in radio cabinets and speakers, decorative woodwork, wall decoration, lampshades and stands, steel office furniture, footwear (shoe heels), pianos, statuary, umbrellas and even hats. The lacquers can either be applied with a brush or in the case of motor finishes with a spray pistol or gun. This is an atomiser worked like a scent spray, only with compressed air. (Plate 32.) The finish being matt like an eggshell is polished with burnishing paste and wax. Cellulose varnishes are being used for reproducing a french polish finish, but it is doubtful if they are as effective and lasting.



[*By courtesy of Imperial Chemical Industries, Ltd.*

Plate 31.—TEASING COTTON BEFORE CONVERTING IT INTO ARTIFICIAL SILK (See p. 242)



[By courtesy of *Imperial Chemical Industries, Ltd.*

Plate 32.—SPRAYING A CAR WITH NITROCELLULOSE LACQUER AT ONE OF MESSRS. BELCO'S WORKS (See p. 258.)

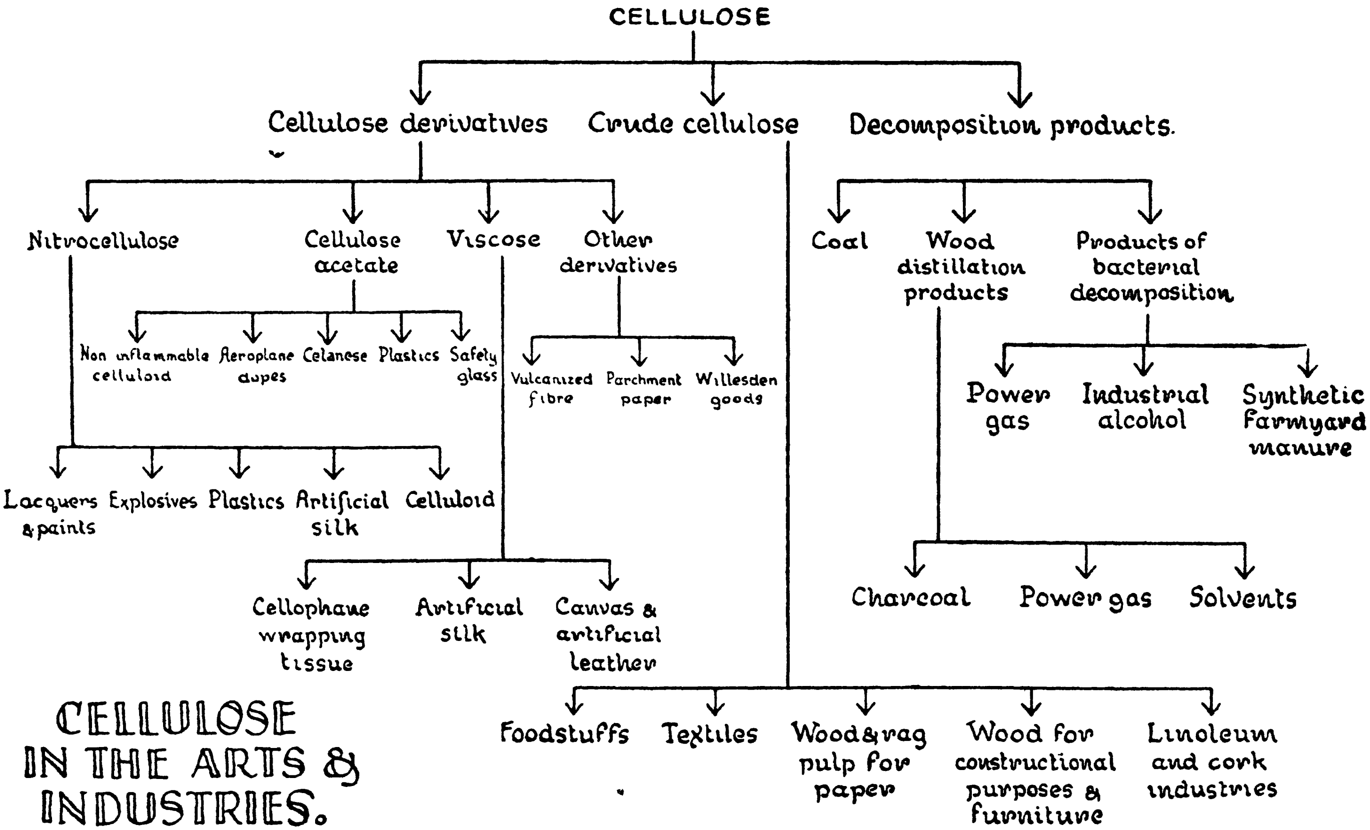

CELLULOSE
Cellulose derivatives
Crude cellulose
Decomposition products.
Nitrocellulose
Cellulose acetate
Viscose
Other derivatives
Coal
Wood distillation products
Products of bacterial decomposition
Non inflammable celluloid
Aeroplane dupes
Celanese
Plastics
Safety glass
Vulcanized fibre
Parchment paper
Willesden goods
Power gas
Industrial alcohol
Synthetic Farmyard manure
Lacquers & paints
Explosives
Plastics
Artificial silk
Celluloid
Cellophane wrapping tissue
Artificial silk
Canvas & artificial leather
Charcoal
Power gas
Solvents
Foodstuffs
Textiles
Wood & rag pulp for paper
Wood for constructional purposes & furniture
Linoleum and cork industries
CELLULOSE IN THE ARTS & INDUSTRIES.

FIG. 40

CHAPTER XI

COLOUR CHEMISTRY

FROM the earliest times colour has exerted an important psychological effect on mankind. It has a very definite place in the scheme of things. When we observe the beautiful colours of both art and nature, and reflect how they contribute to our happiness, we realise how dull the world would be in black and white. Not content with the riot of colour in nature, primitive man imitated it by extracting dyes from plants and animals. We have all inherited this desire for colour, the gentler sex perhaps more so than the stronger, not only in our clothes and surroundings but in our food and drink, and even on our body. The dyeing of the hair and tattooing of the human form have been practised from time immemorial. In an attempt to increase their attractiveness by the application of art, savages still decorate their bodies with pigments obtained from the earth or from the roots, flowers and fruits of plants. Nor can we over-estimate the role that colour has played and still plays in our social life. In ancient times it was a mark of distinction to be born *porphyrogene*, that is, born in the purple, and was equivalent to being born with a silver spoon in one's mouth. It would certainly be a sufficient recommendation for a place in the Debrett of those days. Colour has further been employed in the symbolism of the emotions, patriotism and religion.

Curiously enough when nature requires a permanent colouring, she never uses dyes or stains as man does. Some of the most beautiful colour schemes in nature depend upon diffraction effects, the coloration being due to the effect upon light of a series of fine points, or lines, or fibres, as in the feathers of birds, the wings of butterflies and the wing-cases of beetles.

Two factors determined the development of the art of colouring, namely the action of light and water. A colour must be fast to light, that is, it must not bleach or change shade, and it must withstand washing. The remarkable achievements of ancient Egypt in producing fast colouring matters can be judged from the paintings and mural decorations that have survived several thousand years of hot sun. Man's first dyes were probably the juices of berries and flowers, and the decoctions obtained from coloured woods and tree barks. Either by accident, or by the process of trial and error, he found that the colours from these materials could be "fixed" or made permanent by mixing with earth and clay containing alumina and iron. Thus arose the process of mordanting or fixing the dye in the fibres of the fabric. The ancients brought the use of dyestuffs to a state of perfection; but their dyes were limited to those obtained from herbs, roots, the bark of trees, berries, lichens, insects and shellfish. Tyrian purple, or royal purple, one of the rarest and most highly prized dyes of antiquity, was obtained from a species of mollusc or shellfish (*Murex*) found throughout the Mediterranean.

> Who has not heard how Tyrian shells
> Enclosed the blue, that dye of dyes
> Whereof one drop worked miracles,
> And coloured like Astarte's eyes
> Raw silk the merchant sells?
>
> —*Browning.*

The dye extracted from this sea-snail went to colour the robes of the Cæsars. It is secreted as a thick whitish fluid, smelling of garlic, from a small sac behind the head. When spread upon cloth and exposed to sunlight, an essential part of the process, it changes to light and then deep green, blue and finally purple. If the cloth is washed with soap the alkali in the latter changes the purple dye to a brilliant crimson, Byzantine or cardinal red. Since over thirty thousand of the tiny organisms were required to furnish one ounce of the dye, clothes of purple were beyond the modest purse of the ordinary Roman; in any case, he would not be permitted to wear them. Purple was the symbol of the patrician. Pliny, the Roman writer whose *Historia naturalia* was as well known to antiquity as the Encyclopædia Britannica is to-day, refers to the molluscs yielding Tyrian purple as *purpura,* whence comes our word purple. During recent excavations at Pompeii, an old dye-works was unearthed and in the locality were discovered large quantities of murex shells. It is interesting to note that synthetic Tyrian purple can now be obtained.

Madder or alizarin is another important natural dyestuff that has been employed for thousands of years. Mummy cloths dyed with madder and indigo have been obtained from Egyptian tombs dating back 6,000 years. The more recent discoveries made in connection with Tutankhamen's tomb reveal to us the splendour of the decorative colouring of the craftsmen of the Pharaohs. At this point the reader may be reminded of the legacy that the Celtic and Teutonic races have inherited from the East. As a result of the conquests of Alexander the Great (356–323 B.C.), new dyestuffs were introduced from India to Greece, then to Rome, and finally to the whole of Western Europe. In addition to a knowledge of the arts and crafts much knowledge of a purely cultural value has reached us from Greece. It is also certain that new dyes were introduced when Islam made contact with Europe between the seventh and thirteenth centuries. By the time of the Crusades madder, which had now become known as Turkey red or by its Arabic name of *alizari*, was extensively cultivated in France and Italy. The dye was prepared by drying the washed roots of the madder plant in the sun and grinding them to a fine powder.

In the thirteenth century Venice became the centre of the European dyeing industry. The first European book on dyeing, *Mariegola dell arte de tentori*, was published there in 1429. The supremacy of Venice was overthrown when Columbus discovered America towards the end of the fifteenth century and a new route to India via the Cape of Good Hope was opened up. This not only facilitated the transportation of dyestuffs from the Orient to Europe but many new dyes were imported from the New World, among them cochineal and logwood. Cochineal, a carmine dyestuff made by robbing the female insect, *Cacti coccus*, of her coat, is still extensively used as a colouring matter. It was once employed for dyeing the red coats of our soldiers.

In 1630 a great improvement took place in the dyeing industry. In that year a Dutch chemist named Cornelius Drebbel discovered that brilliant scarlets could be obtained by dyeing with cochineal and a tin salt as a mordant instead of alum. We have previously mentioned that some dyes cannot be applied directly to a fabric. This must first be soaked in a solution of a certain metallic salt, termed a mordant, before going into the dye-bath. The mordant serves to attract the dye, combines with it, and fixes it firmly to the fabric. Mordant dyes have recently undergone a rapid development, especially in dyeing cotton fabrics, and tin compounds have been found to be extremely useful mordants. Salts of aluminium, chromium and iron are also used. By their means we can obtain not only beautiful and fast colours but substances which are not in themselves dyes can be made to produce coloured fabrics.

During the seventeenth century Coventry was noted for its blue dyed cloth, which the Puritans adopted and referred to as "Coventry true blue", as distinct from the scarlet worn by Charles I and his followers. From the sixteenth century until the reign of Charles II there was much prejudice against the use of logwood and indigo in this country, the opposition coming chiefly from the woad cultivators who persuaded the Government to prohibit the use of foreign dyes. The introduction of printed calico and chintzes in 1700 met with a similar opposition from the silk, wool and linen industries. The present British dye industry is also "protected".

Indigo is one of the oldest and fastest of dyestuffs. It has long been produced in India from the juice of several plants of a certain species allied to the woad plant, from which the early inhabitants of this country obtained a blue dye for their personal adornment. Woad is still produced in Yorkshire for certain dye processes. The juice of the indigo plant is colourless, but on exposure to air it rapidly darkens and forms the blue dye that we call indigo. Ever since its introduction it has been highly valued as a dye because it is fast to light, air and water. During the Middle Ages some difficulty was naturally experienced in obtaining the dye from India and woad was cultivated in Europe, especially in Germany, to replace it. When the link between Europe and India was strengthened and trade developed, the Indian product dominated the markets of the world, until the chemist decided that the products of nature's laboratory—or at any rate many of them—could be quite successfully reproduced in the retort and test tube. The synthetic production of indigo has now ousted the natural product from the market.

For thousands of years and until the middle of the last century all the dyes employed were of natural origin. Although the art of dyeing was purely empirical and the processes employed were laborious, tedious and little understood, the skilled dyer could turn out a variety of products with a comparatively large number of shades. During the last century the energies of chemists were devoted to the synthetic production of naturally occurring compounds with the result that many industries were revolutionised. The dyeing industry was not exempt. Man no longer wished to depend on the beautiful colours made in the laboratory of nature; he wanted to analyse and imitate them. He took to pieces the dyes made in the factories of the plant cell, identified the fragments, and attempted to put them together again. Thus were the first dyes synthesised.

In the first chapter of this book we saw how the idea once prevailed that animal and vegetable, or organic, substances were different from inorganic ones, and that they were built up in the living organism under the influence of a mysterious vital force. It was further held that on this account it was impossible to synthesise them or build them up in the laboratory. After Wöhler's synthesis of urea in 1828 these views were gradually abandoned, although they died a lingering death. Eventually it was realised that organic substances obey ordinary chemical laws, and an impetus was given to the development of organic research. Chemists analysed larger numbers of organic substances, and having ascertained their constitution, that is the manner in which the constituent atoms are arranged in the molecule, they commenced to build them up from their elements. The chemist has dismembered the molecules of the historic vegetable dyestuffs, indigo and madder, and step by step he has built them up in the laboratory from comparatively simple substances. Many dyes have been discovered that are unknown in nature; in fact the majority of the dyes employed to-day are artificial creations. The advantage of synthetic dyes over those supplied by nature lies in their purity, variety and adaptability. The dyeing properties of many of the natural products were often due to constituent parts, and it was difficult to get a standardised dye.

What is the source of the chemist's rainbow? It comes from coal, or to be more exact from coal-tar, that dirty, evil-smelling liquid formed when coal is distilled. For many years coal was distilled exclusively for the gas and coke; the tar was given away or even dumped on neighbouring land and in streams. One of the most useful things in the world went begging. Yet from it the chemist now obtains drugs, explosives, perfumes and all the colours of the rainbow. The wonders of this remarkable liquid have been extolled by that humorous weekly, *Punch*:

> There's hardly a thing that a man can name
> Of use or beauty in life's small game
> But you can extract in alembic or jar
> From the "physical basis" of black coal-tar—
> Oil and ointment, and wax and wine,
> And the lovely colours called aniline;
> You can make anything from salve to a star
> If you only know how, from black coal-tar.

One chemist has compared coal-tar to the magic purse of Fortunatus, from which anything wished for could be drawn. Foul-smelling and dingy as it is, coal-tar can yield the sweetest perfumes and the most brilliant dyes. Bishop Berkeley, a divine of the eighteenth century who wrote a dissertation on the virtues of tar-water, thought that it contained the quintessence of the forest, the purified spirit of the trees, and that therefore it could cure man of all the ills to which he is heir. Unfortunately the latter view has proved to be erroneous, but there is no doubt that tar *is* the quintessence of the forests of bygone ages. It is convenient at this stage to explode the hoary legend that coal-tar contains colouring matters ready formed; that they may be seen floating about on the surface of the liquid; and that the attention of Perkin, the discoverer of the first synthetic dye, was attracted to the subject by observing the beautiful colours exhibited by a film of tar floating on water. Such colours are, of course, given by all thin films. One might as well attempt to extract dyes from soap bubbles or crystal glass. From coal-tar to dyes is a long step. When the tar is redistilled about seven important "crudes" are obtained—

benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene—and these are the materials that serve as the starting point in the preparation of dyes. They are converted into "intermediates" by the replacement of some of their hydrogen atoms by other atoms or groups, e.g. nitro-groups. For the most part these intermediates are colourless substances or slightly yellow. On further treatment with various substances the structure of the molecule becomes more complex and we then produce a dye.

We cannot hope to understand the chemical changes that go on during the production of dyes without once more referring to the formulae or working models of the chemist. Although the first synthetic dye was prepared in 1856, no real progress was made in the subject until the constitution of benzene and its derivatives was ascertained. The chemist tries to visualise what goes on during chemical reactions by means of formulae; they are working models of molecular architecture. The idea of molecular structure has played a very important part in the progress of organic chemistry. Long before synthetic dyes were thought of chemists knew that each molecule of benzene consisted of six atoms of carbon and six atoms of hydrogen, but nobody was quite sure how they were arranged or linked together in the molecule. And then, in 1865, there occurred one of the most famous rides in history. It was made on top of an omnibus by the German chemist Kekulé, during his stay in London. One summer evening he decided to take a ride on the top of an omnibus from Islington to Clapham, and feeling sleepy he soon dropped off into the land of molecules. To quote Kekulé himself:

> One fine summer evening I was returning by the last omnibus through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo! the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion, but up to that time, I had never been able to discover the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller, whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain. . . .

Eventually Kekulé awoke and, arriving home, spent part of the night putting on paper sketches of these dream forms. From these he evolved a system of constitutional formulae to represent the molecular architecture of organic compounds. When Kekulé was in Ghent, he had another dream. He dozed over the fire in his study while thinking about the formula of benzene. He saw the carbon and hydrogen atoms dancing like imps in the flames and on the carpet, and from his half-closed eyes he saw chains of atoms squirming and twisting in a snake-like whirl.

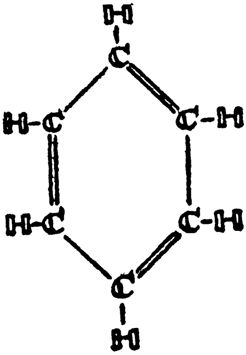
> But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke.

The picture of the snake swallowing its own tail gave Kekulé the idea of what chemists now call the benzene ring. No chemical theory, unless it be Dalton's, has been more fruitful and provocative of research. Kekulé remarked:

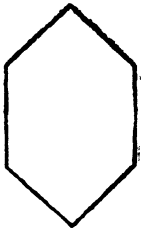
> Let us learn to dream, then perhaps we shall find the truth. But let us beware of publishing our dreams before they have been put to the proof by the waking understanding.

The disciples of Freud, who have carefully analysed Kekulé's dreams, declare that he was morally guilty of the crime of Œdipus!

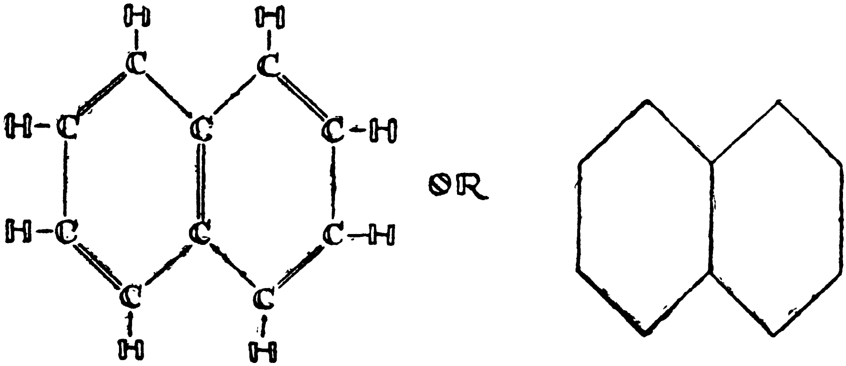
Following Kekulé's dream, the formula for benzene is obtained by linking up in a ring six carbon atoms, to each of which a hydrogen atom is attached—



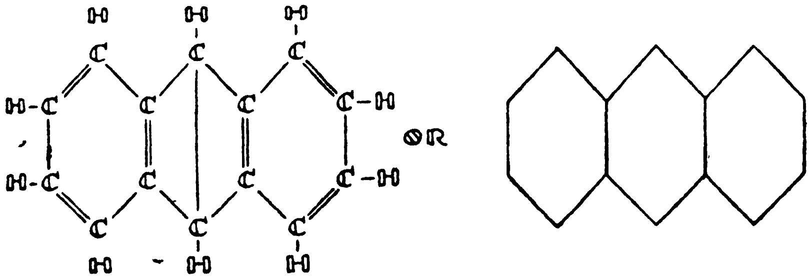
or for the sake of simplicity just the skeleton,



bearing in mind that each corner of the hexagon or benzene ring is occupied by a carbon atom linked to a hydrogen atom. There are two types of carbon compounds, open chain or *aliphatic*, and closed chain or *aromatic* compounds. Benzene and its derivatives belong to the latter. Naphthalene and anthracene, two other important sources of dyes, consist of two and three benzene rings linked together—

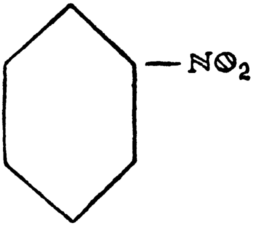


Naphthalene

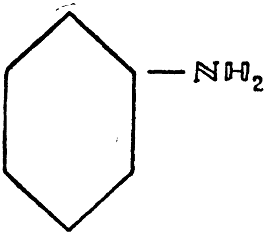


anthracene

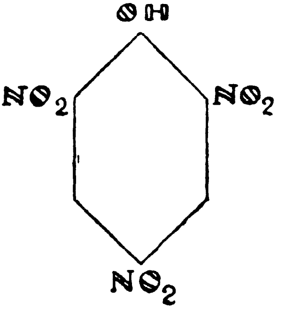
By treating benzene with nitric acid, one of the hydrogen atoms is replaced by a nitro-group and we get nitro-benzene, $C_6H_5NO_2$, or



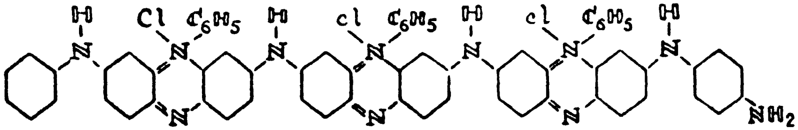
This on treatment with iron and hydrochloric acid—a mixture generating hydrogen—yields aniline,



which is not a dye. It is, however, the source of a large number of colours which are commonly called "aniline dyes". The NH_2 group in the above formula is known as the "amino" group; it is present in many dyes. Other dye intermediates are obtained by fixing other groups, such as the hydroxyl group (OH) or sulphonic acid group (HSO_3), on to the hydrocarbons benzene, naphthalene and anthracene. These hydrocarbons are the starting point in the preparation of all synthetic dyes. Intermediates for the most part are not coloured; they are converted into dyestuffs by further treatment. Thus phenol, which is colourless, yields on nitration the yellow picric acid,



which is used to a limited extent as a dye, although it is more important as an explosive. Dyestuffs can also be prepared by linking together, or condensing as the chemist terms the process, molecules of intermediates. About three hundred intermediates are known and they furnish over five thousand dyes, of which only about a thousand are in use. Some dyes such as picric acid, are comparatively simple. Others, such as aniline black, are extremely complicated bodies. Aniline black is



Many of them with outrageously long and incomprehensible names pass under quite unassuming titles in the trade. Thus 3:7 dimethyl-2:8 diamino-10-phenylphenazonium chloride is called Safranine L. Only a dye expert would know what the dye was from its trade name. But given its formula name the chemist can see from what it is made and even how to make it.

Seventy-five years ago (1856) William Perkin was carrying out research during his Easter vacation on the synthesis of quinine from coal-tar products. He obtained no quinine but he discovered a fertile and untouched territory, namely the land of the aniline dyes. It is said that as a boy Perkin was very precocious. When a schoolboy at the City of London School he would bolt his lunch in order to attend dinner-hour chemistry lectures. At fifteen he sat at the feet of Hofmann, the professor of chemistry at the Royal College of Chemistry, and commenced research when only seventeen. Hofmann set young Perkin on the isolation of the hydrocarbon phenanthrene from coal-tar, and the synthesis of quinine. Such a task would be heartily condemned by modern educationists; to-day boys of such tender years have scarcely passed their Matriculation examination. So eager was Perkin on the research that he set up a laboratory of his own where he could work during the vacations. It was while working in his private laboratory during the Easter of

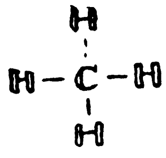
1856 that he oxidised aniline with potassium dichromate and sulphuric acid, and obtained a black tarry mess. The average investigator of the day would have probably thrown this away. But Perkin exhibited the true research spirit. He extracted the black residue with alcohol and found that it gave a beautiful purple solution. This was *Mauve* or *Mauveine,* the first synthetic dye. While Perkin is rightly credited with the discovery of this he was not the first to make organic substances that were capable of colouring fabrics. In the eighteenth century picric acid had been obtained by treating indigo with nitric acid and in 1834 Runge had discovered rosolic acid or aurin in coal tar. Neither process was of any practical importance. Indigo was a better dye than the picric acid obtained from it, and aurin could not compete in price or quality with the naturally occurring colouring matters.

Curiously enough, when Perkin repeated this experiment with pure aniline he could not obtain the dye. It was only because the aniline that he used originally was impure—it contained some toluidine—that he discovered mauve. In those days the benzene was far from pure and contained varying quantities of the hydrocarbon, toluene, $C_6H_5CH_3$. This accounted for the toluidine, $NH_2.C_6H_4.CH_3$, as an impurity in the aniline. Perkin followed up his discovery by showing that mauve could be used for dyeing silk a shade fast to light and washing. The French dyers took to Perkins' new colour—at their suggestion it was called *mauve,* the French for the mallow-flower—and they made its manufacture a commercial success. A year later Perkin left the Royal College of Chemistry, and with his brother and father commenced to make the dye on a large scale at Greenford, near Harrow. Although to-day Perkin's mauve is mainly of historical interest, it was used for many years for colouring postage stamps. This and a knighthood were the only honours bestowed upon the chemist whose research paved the way for the coal-tar colour industry.

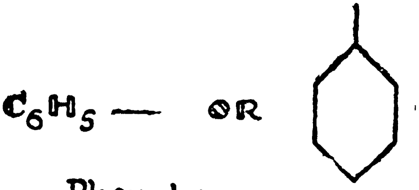
With Perkin's discovery of mauve and the introduction of a rational system of formulae and nomenclature, the discovery of new dyes followed quickly. Chemists in England and on the Continent directed their attention to coal-tar products and to the preparation of dyes from them. Shortly after Perkin's epoch-making work, Hofmann discovered that crude aniline could yield a red dye if treated with oxidising agents other than potassium dichromate. This led to the discovery of the dye *Magenta* (fuchsin), or *Aniline red*, in 1858. It is the salt of a base known as rosaniline. Nicholson's discovery of a suitable oxidising agent, arsenic acid, enabled magenta to be made on a large scale in all the chief colour factories of Europe. In four years the accidental discoveries of Perkin and Hofmann, made in the course of purely abstract chemical research work, developed into an important branch of chemical technology. Aniline was made in larger quantities than ever before. The reader will now realise that dyes are not present ready-formed in coal-tar; nor are they present in or formed by the mixing of dye intermediates. They are formed from the latter by a series of chemical changes.

It was soon discovered that magenta could, by further chemical change, be converted into a large number of dyes. Thus in 1860 two French chemists, Girard and De Laire, observed that on heating rosaniline—the base of magenta—with aniline and an aniline salt, blue and violet colouring matters were formed. This resulted in the manufacture of *Aniline blue*. At first it had only a limited application because it was only soluble in spirit and not water. Shortly afterwards, however, Nicholson discovered that it could be made soluble in water and alkalies by sulphonation or treatment with strong sulphuric acid. In 1862 Hofmann prepared violet colouring matters by the action of methyl and ethyl iodides on rosaniline; these were known as *Hofmann's violets*. During the formation of magenta by Nicholson's process other dyes are formed in small quantities. Among them are *Phosphine* or *Chrysaniline*, discovered by Hofmann in 1862, and *Safranin*, which was isolated by Perkin himself in the next year.

The chemists of this period were not content with just making new dyes; they had to determine their constitution. Chemistry is a philosophic as well as a creative science. One of its fundamental problems is to find out the number and kind of atoms present in different compounds and the manner in which they are arranged. When this has been accomplished the chemist says that he knows the constitution or structure of the molecule of the compound. To institute a simple analogy, suppose we have a given number of bricks, slates and beams, and put them together to make a house. By arranging the materials in different ways we could build an almost indefinite number of houses, but they would all have the same "composition", that is the same number of bricks, slates and beams. In the same way, the molecules of organic compounds, including those of dyes, are made up of several different elements, but the number of ways in which they can be arranged is legion. The structure or constitution of the molecule would be different in each case. Hofmann first studied the chemistry of magenta. He showed that it could be readily converted into rosaniline, the structure of which remained obscure for many years. After a large number of chemists had attempted to elucidate the problem, the ground was cleared in 1878 by Emil and Otto Fischer, who determined the constitution of rosaniline by preparing it from its parent hydrocarbon, *triphenylmethane*. Now we know the constitution of this; it is methane, CH_4, with three of the hydrogen atoms replaced by three phenyl groups, or three benzene rings, each of which has had one hydrogen atom removed.

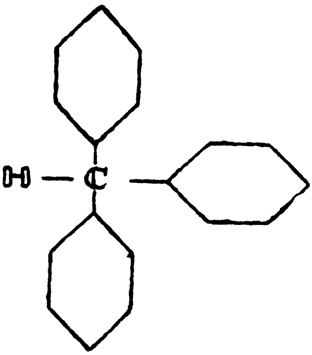


methane

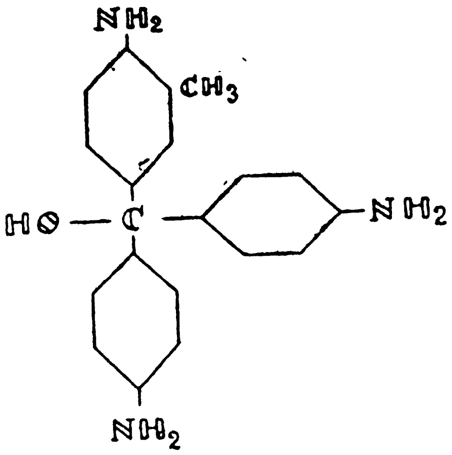


Phenyl group

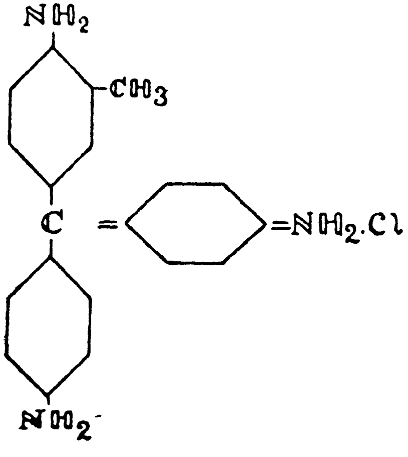
Hence triphenylmethane is



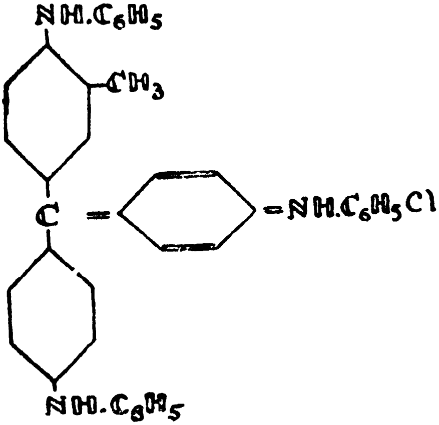
and rosananiline, the base of magenta, is


NH₂
CH₃
HO — C
NH₂
NH₂

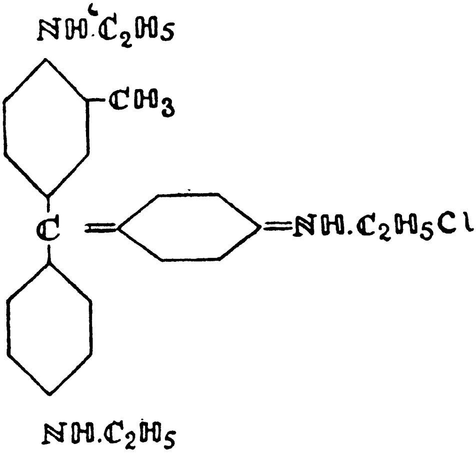
The compound of this with hydrochloric acid is magenta itself—


NH₂
CH₃
C =
=NH₂.Cl
NH₂

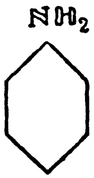
Aniline blue results from the displacement of a hydrogen atom in each of the three amino groups (NH_2) by phenyl groups (C_6H_5)—



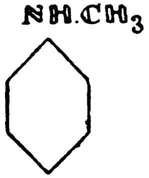
In Hofmann's violet one of the hydrogen atoms of each NH_2 group of rosaniline is replaced by an ethyl group (C_2H_5)—



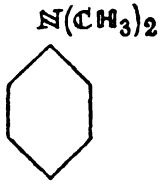
By the methylation and ethylation of rosaniline Hofmann produced violet colouring matters. Since rosaniline is obtained by the oxidation of a mixture of aniline and toluidine, it is reasonable to suppose that if the latter mixture be first methylated and ethylated and then oxidised it will also give violet dyes. Lauth obtained violet dyes by this method in the early 'sixties. Methylated anilines are now important intermediates in the manufacture of dyestuffs. Either one or both of the hydrogen atoms of the NH_2 group in aniline can be replaced by methyl groups (CH_3) to form respectively methyl aniline and dimethylaniline.



Aniline

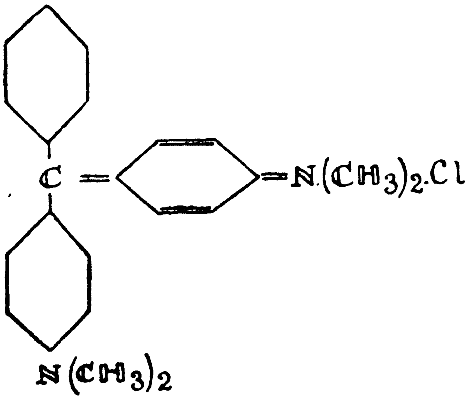


Methylaniline



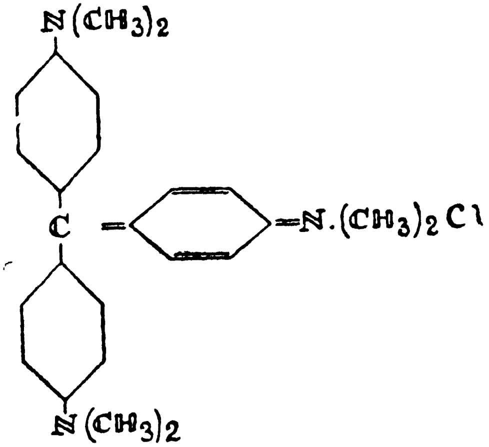
Dimethylaniline

In 1878 Döbner obtained a brilliant green colouring matter termed tetramethyldiaminotriphenylmethane chloride, more commonly known as *Malachite green* or *Benzaldehyde green*, by the action of dimethylaniline on a product obtained by chlorinating toluene. These long words are not really words; they are condensed formulae. Malachite green is just a handy name, but does not mean anything. The formula word, puzzling as it is to the uninitiated, simply tells us that the dye has the following structure—



and even suggests that it can be made from dimethylaniline.

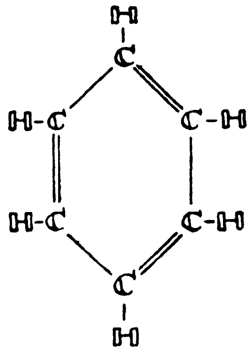
Caro and Kern discovered that dimethylaniline and analogous compounds react with phosgene, ($COCl_2$)—a compound of chlorine and carbon monoxide—to form brilliant violet and blue dyes. Crystal violet, one of these, is hexamethylrosaniline, or rosaniline with six of its hydrogen atoms replaced by methyl (CH_3) groups.



The search for new dyestuffs and the elucidation of their structure continued without interruption. Not only were synthetic dyes obtained that had no counterpart in nature, but in due course the synthesis of naturally occurring dyestuffs was accomplished. In 1869 Perkin, and independently Graebe and Liebermann, succeeded in preparing from anthracene a dyestuff termed alizarin, which was identical with the colouring matter present in the madder root. This discovery precipitated an economic crisis in the madder industry. In a few years the madder fields of Europe disappeared and nearly every country became dependent on Germany for the synthetic dye. This success encouraged chemists to devote much time and expense to the synthesis of indigo. The best brains of Europe were pooled to accomplish this, and although Baeyer prepared the dye from coal-tar intermediates in 1880, technical success was not achieved until seventeen years later.

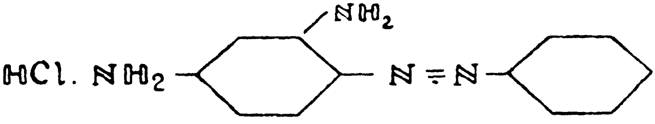
It was soon found that the synthetic dyes were superior to the naturally occurring ones. Art can improve on nature in this direction. The synthetic products are more numerous, purer, more reliable in shade and considerably cheaper than the natural ones. Natural indigo, for example, contains from forty to eighty per cent of impurities; the manufactured dye can be standardised to any strength and shade, and for this reason is preferred by the dyers. But for at least twenty-five years after the founding of the new industry, the dyers were hampered by the fact that nearly all the new dyes could be applied directly to animal fibres such as wool and silk, but not to cotton. This had to be specially prepared first. Consequently the discovery of direct cotton dyes was of great importance in the dyeing industry. In 1884 the German chemist, Bottiger, prepared *Congo red,* the first direct cotton dye. It was not very fast, but the determination of its constitution enabled other direct cotton dyes to be manufactured.

Why do certain organic compounds appear coloured? Colour is, as we know, a sensation caused by the stimulating action of light on the optic nerve. Although we are still ignorant of the real cause of colour in organic compounds, chemists are agreed that it is very closely related to the way in which the atoms in the molecule are joined together and to the presence of certain atomic groupings. Not all coloured substances are dyes. A dye, as distinct from a coloured body, must not only be strongly coloured in itself or produce a colour with a mordant; it must be capable of fixing itself on to the fabric to form a colour that will withstand air, water and light. Its degree of permanency when subjected to these agents is known as "fastness". There is always some kind of intimate physical or chemical union between the dyestuff molecules and those of the textile fibres. The kind of light reflected by the latter depends upon the molecular architecture of the dye. It is significant that all dyes contain carbon atoms linked together in the form of a ring, as in benzene, and that some of the atoms are *unsaturated,* that is, they do not link up with their full quota of neighbouring atoms. A carbon atom can normally attach itself to four other atoms or groups of atoms—we say it has a valency of four—but in certain compounds such as benzene some of the carbon atoms do not join up with this number of other atoms or groups. These compounds are said to be *unsaturated*; they readily take up more atoms to become saturated. Benzene is unsaturated—



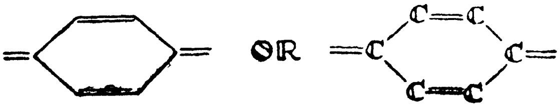
because each carbon atom has not got four other atoms linked to it. We put double linkages (=) in the formula to show that the carbon atoms are unsaturated. Since the latter, having less than their proper number of links, are not held sufficiently tight, they can rattle like a machine does when it has a few nuts or bolts loose. This vibration is bound up with the property of absorbing and reflecting light waves of a certain frequency of vibration; in other words, it is bound up with colour. Benzene absorbs light rays of very short wavelength—the ultra-violet rays—but does not reflect any visible rays and therefore appears colourless to us. Bodies that reflect all the white light striking them appear colourless or white; others that reflect none of the light are black; while those that absorb light rays of certain wavelength and reflect the others appear coloured.

If, however, we introduce other groups of atoms into the benzene ring and make the molecule larger, the light rays that are absorbed drop into the visible spectrum, and we have a coloured substance, if not an actual dye. This is because the group attached damps down the rate of vibration of the benzene molecule and makes it absorb light waves of lower frequency. Now once the colour-producing body has been formed, the colour can be altered by attaching other atoms or groups of atoms to it. For example, it will be remembered that red magenta is converted into aniline blue by the introduction of phenyl groups, or into methyl violet by the introduction of methyl groups. Similiarly amino (NH_2) and hydroxyl (OH) groups give other colours. Such colour-producing groups are known as *auxochromes*. The groups of atoms that are the actual source of colour in the molecule are known as *chromophores*. For example, in a certain class of dyestuffs known as the *Azo-colours* the *azo-group*, —N=N—, is the chromophore. This is present in chrysoidine,



one of the simplest dyes of this class. In addition to the chromophore, the molecule must contain a basic group, such as NH_2, or an acidic group, such as OH or HSO_3, before a dyestuff is formed. Both chromophores and auxochromes produce dyes when introduced into certain compounds called chromogens. These are all compounds which contain the group C_6 arranged as in benzene and they are unsaturated.

In the formulae of magenta and the triphenylmethane dyes (pp. 274–5) one of the benzene rings has the form



This is known as the *quinonoid* form of benzene and it is generally considered that all dyestuffs possess a quinonoid structure. Many dyes that are basic or acidic are colourless in themselves and only form a true dyestuff on treatment with an acid or alkali. This is because the structure of the original substance is changed into the quinonoid form by the latter.

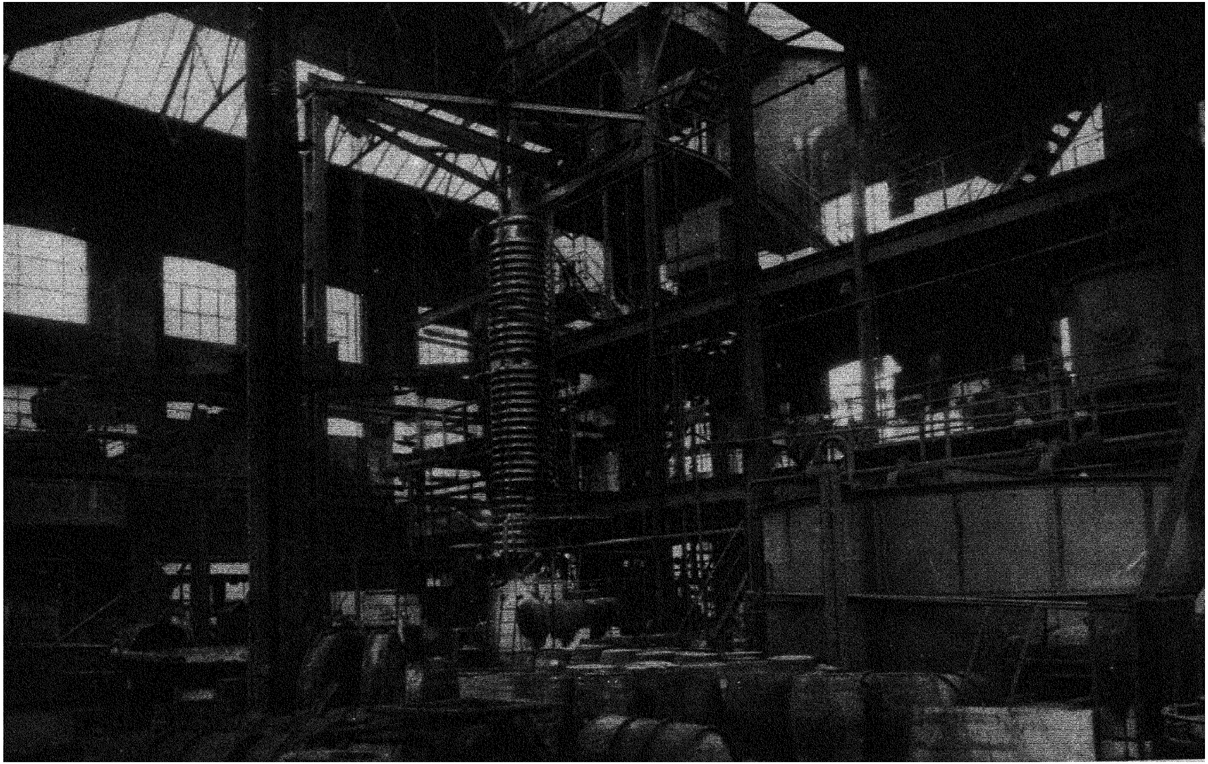
Summarising, we can say that while the hydrocarbon framework of dyestuff molecules is primarily responsible for the production of colour, the shade and fastness depend upon certain groups of atoms attached to the framework. The chromophore groups determine the chemical class to which the dye belongs and the salt forming, or auxochromic groups (NH_2, OH, etc.), are responsible for the dyeing properties, and resistance towards light, air and soap.

Dyes vary in the manner in which they are applied to fabrics. Some can be used directly by merely soaking the fabrics in a solution of the dye. They are called *direct* or *substantive* dyes and dye cotton and artificial silk (not celanese) from alkaline or neutral baths, or animal fibres, such as wool and silk, from an acid bath. Such dyes are largely employed for cotton printing and dyeing, and for colouring artificial silks of the viscose type. A special range of dyestuffs termed *Icyl colours* has been introduced for dyeing cuprammonium silk. Other dyes require to be fixed on the fibre with certain metallic salts or mordants, which are usually salts of aluminium, chromium, iron or tin. The fibre is impregnated with a solution of the mordant and dipped into a bath of the dye, which is attracted from solution and forms an insoluble compound, or *lake*, with the mordant in the fibres themselves. For calico printing a solution of the dyestuff suitably thickened and mixed with the mordant, usually chromium acetate, is printed on the material and the latter steamed. The heat promotes reaction between the dye and mordant, and a coloured lake is deposited in the fabric.

Some dyes are basic in character, that is they form salts with acids. Mauve, magenta and most of the triphenylmethane dyes are of this type. They can be applied directly to wool, silk, leather and feathers, but require a mordant for fixing on cotton. This is because wool and animal matter contain acid groups that combine with these dyes, whereas cotton is perfectly neutral and has no affinity for them. The basic dyes are employed in calico printing, for preparing wall-papers, and for colouring oils and varnishes. The acid dyestuffs are similar in their dyeing properties, although of course they are acidic, not basic, in character. They can dye silk and wool directly from an acid bath, but they are not suitable for cotton and vegetable fibres.

Then there are some dyes, such as indigo, aniline black and the indanthrenes, that may be developed in the fibre. Indigo and the indanthrenes are known as vat dyes. They are first of all made into soluble but colourless bodies, and in this condition are applied to the fabric. On hanging this in the air, the now colourless dye is slowly oxidised into the coloured but insoluble variety, and remains firmly attached to the fibres of the fabric. Aniline black is prepared in the fabric by soaking it in a preparation of aniline and an oxidising agent (potassium chlorate), with a trace of a catalyst (iron or copper) to facilitate oxidation. On passing the fabric between heated rollers, the aniline is oxidised to aniline black, which is deposited in the fibres of the material. The fastness of the dye to light, air, soap and destructive agencies cannot be surpassed by any other colour. Although it can only be applied to cotton, it is remarkable that half the world's total production of aniline is used for the production of this dye. John Lightfoot, a dyer of Accrington, accidentally produced the dyestuff in 1863 during some experiments on the printing and dyeing of cotton goods. Bearing in mind Perkin's experiment he oxidised aniline, but with potassium chlorate instead of potassium dichromate as Perkin had done, and attempted to print the mixture on cotton with a wooden block. But little or no colour developed. When, however, the mixture was printed out with a copper roller a green colour appeared. Lightfoot correctly attributed the formation of the latter to the catalytic action of the copper in the roller, and by using copper salts as catalysts he was able to produce quantities of a fast black dye. Many of the so-called romances of chemical industry are purely fictitious; a large number of the discoveries have been either accidental or the result of the application of "pure" scientific discoveries.

Why does a dye attach itself to a fabric? The solution of this problem is intimately bound up with the chemical composition of not only dyes themselves, but of the wool, silk and cotton which form the fibres of most fabrics. The mechanism of mordant dyeing should be quite clear to the reader; dye and mordant meet in the fibres of the fabric and produce an insoluble compound, a lake, in the fibres themselves. But how do dyes attach themselves to wool, silk and cotton without a mordant, and why is it that some dyes will attach themselves to animal fibres (wool and silk) but not to vegetable fibres? Wool and silk are mainly composed of those complex nitrogenous bodies, the proteins, which have as it were a dual personality. Sometimes they will act as acids, and sometimes as bases, a base being a substance that will destroy the properties of an acid and give rise to a new compound called a salt. The protein molecules, then, contain both basic and acidic groups

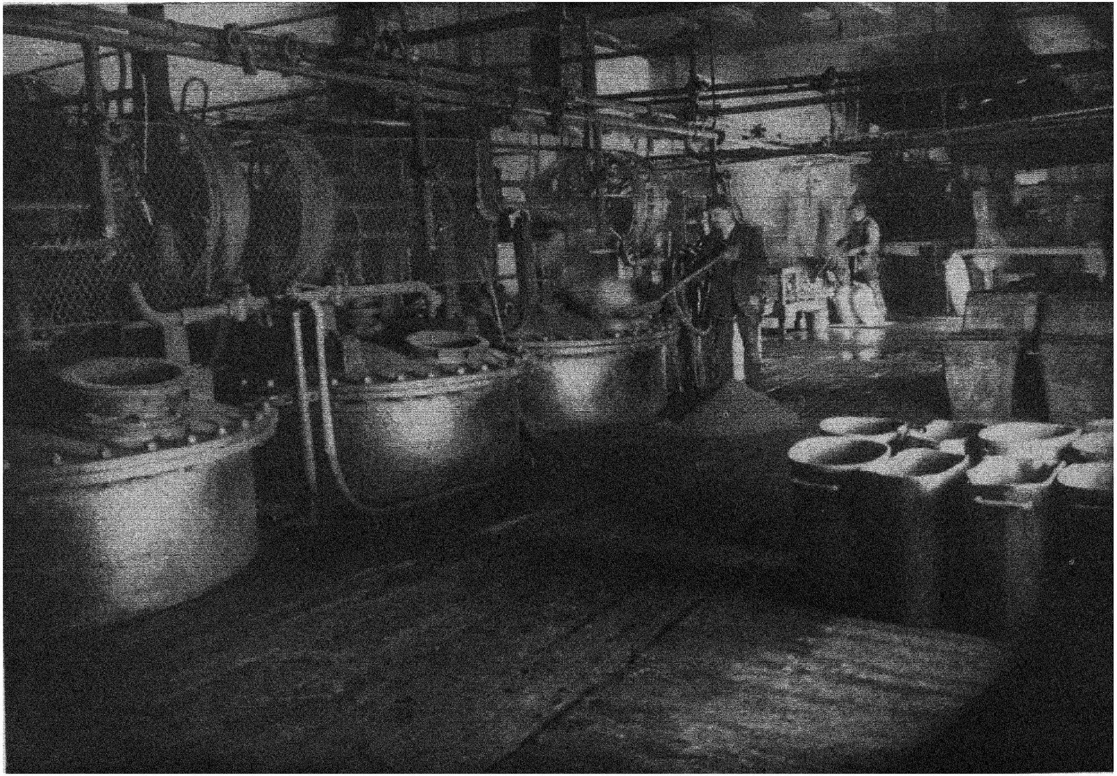


[*By courtesy of Imperial Chemical Industries, Ltd.*

Plate 33.—A STILL HOUSE IN A DYE WORKS

Here "crudes" and intermediates are purified by distillation.

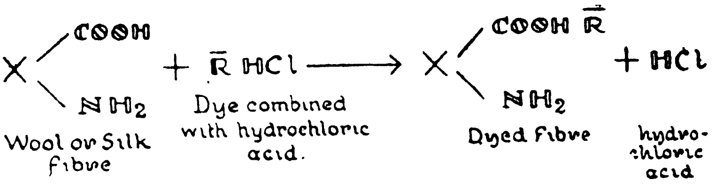
(See p. 265.)



[*By courtesy of Imperial Chemical Industries, Ltd.*

Plate 34.—REDUCTION PANS IN THE INTERMEDIATES DEPARTMENT AT THE BLACKLEY WORKS OF IMPERIAL CHEMICAL INDUSTRIES, LTD.

of atoms. All protein molecules contain amino groups (NH_2), which are the basic ones, and carboxyl groups (COOH), which are acidic. Thus proteins can either form salts by the acid carboxyl group combining with bases, or by the basic amino group combining with acids. We have seen that some dyes have an acidic and others a basic character, and it is these dyes that combine with silk, wool or other animal fibres to give a coloured product. Magenta, for example, is the salt of a basic dye—it is a compound of the base rosaniline and hydrochloric acid—and when it dyes wool or silk the colour base, rosaniline, leaves the hydrochloric acid with which it is combined and attaches itself to the carboxyl group of the proteins of the wool or silk. This can be represented diagrammatically—



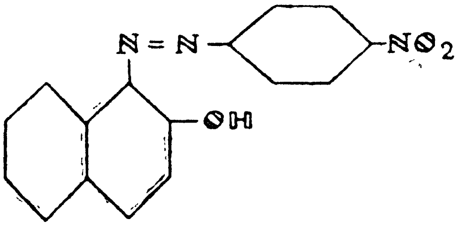
A similar explanation serves for other basic dyes. If, on the other hand, wool or silk is dyed by means of an acid dye, such as picric acid, the acidic groups of the latter unite with the basic amino groups of the proteins of the wool and silk fibres, and the dye is firmly retained by the latter.

The process of dyeing is slightly more complicated than the above explanation would suggest. Microscopic examination of wool and silk fibres has shown that they are capable of *adsorbing*, or condensing on their porous surfaces, layers of the dyestuff which is thus removed from the dye-bath. This action resembles that of charcoal removing the natural colouring matters from syrup in sugar refining. It would appear that the dye is first attracted to the fibre by a kind of surface attraction, or adsorption, and that it then enters into chemical combination with the acidic or basic groups of the proteins composing the fibres. That the combination is only a loose one is proved by the fact that certain solvents, such as alcohol, can remove some dyes from dyed fabrics.

Linen and cotton are vegetable fibres and since they consist mainly of cellulose, they possess neither acidic nor basic characters. Many dyes can only be applied to such fibres with a mordant, but a certain range of direct cotton and linen dyes has been available since the discovery of Congo red in 1884. The direct application of these dyes to vegetable fibres probably depends upon the fact that these are hollow, and that some of the dye gets imprisoned inside them and is held there by the surface action of the cellulose. No lake is formed as with a mordant.

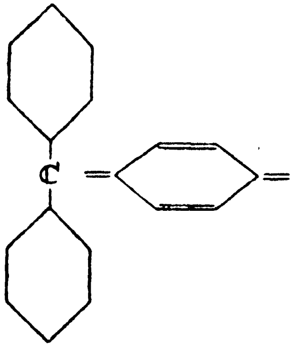
Chemists are able to classify dyestuffs not only according to their behaviour towards the various textile fibres, but also in accordance with the atomic groupings that they contain. Indeed, the most satisfactory classification of dyes is according to their molecular architecture. There are certain dye families, the members of which possess specific group characteristics, although of course the individual dyes may vary widely in colour. Each family name signifies a special type of *molecular* grouping. Thus the dyes of the azo family, and there are over five hundred of them in use, all contain the *diazo group* ($-N=N-$). They are made from aniline and other substances containing the amino group (NH_2). This is "diazotised", that is the two hydrogen atoms are replaced by a nitrogen atom, and the product "condensed" or "coupled up" with a phenol or another substance containing one or more amino-groups. The azo-dyes may therefore be regarded as being made up of two components—the diazotised amino-compound and the substance that it couples with. Peter Griess, chemist to a Burton firm of brewers, first produced these dyes in 1864. They were not marketed until twelve years later. Almost any colour can be obtained with these dyes from yellow, red, brown, to blue, violet and black. The latter shades are formed by using naphthalene derivatives as the coupling compounds. Azo-dyes are employed to colour wool, silk, cotton, leather, wood, food and confectionery.

The azo-group may be present in the molecule once, twice, or three times, and with increased molecular complexity the colour becomes deeper. Dyes with one azo-group are comparatively simple in structure, e.g. *Para red,*

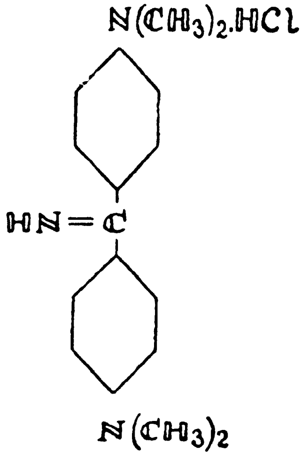


which is the cheap red of pillar boxes and fire engines. As a rule azo-dyes are formed in solution and are salted out, dried and ground. But frequently, insoluble dyes are prepared on the fabric—as in the case of Para red—by steeping cotton in a solution of the coupling chemical and then passing it through a solution of the diazotised amino-compound. Such deposited dyes are resistant to washing, bleaching and light. Another important property of the azo-dyes is utilised in obtaining white effects on coloured backgrounds. The dyes can be made colourless by treatment with a substance known as sodium hyposulphite, and if cotton or silk materials that have been dyed dark blue or other shades with an azo-dye are printed with a preparation of this chemical and then steamed, the colour is discharged on the printed parts of the fabric, leaving a white pattern on a coloured background. Some azo-dyes are spirit-soluble and are used for colouring stains, varnishes and petrol. Others, the *Ionamines* and S.R.A. colours (p. 294), have been specially introduced to dye acetate silk.

The triphenylmethane family, as we have seen, has important historical associations. Most of the early synthetic dyes belonged to it. The dyes of this class are derivatives of benzene, and they all contain the fundamental grouping

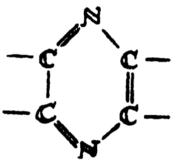


Most of the dyes exhibit brilliant and intense shades of red, violet, blue and green. They have basic, acidic or mordant-fixing properties according to their auxochrome groups. As a class they are not very fast to light. Magenta is used to dye cotton, wool, silk and leather, and like methyl violet and malachite green it is employed as a microscopic stain. Malachite green is used to colour oils, fats and waxes. The most largely used of the basic yellow dyes is *Auramine*,

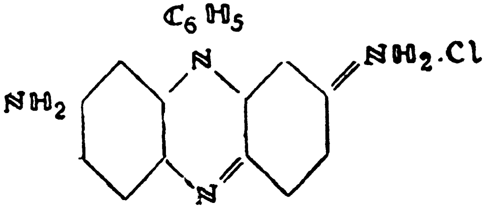


Cotton goods are dyed with it. It gives a pure yellow, fairly fast to light and soap. The basic triphenyl-methane dyes have a powerful toxic and antiseptic action, and for this reason they have found an important application in antiseptic surgery, e.g. auramine is used in eye operations. *Brilliant green*, a dye with a composition similar to that of malachite green, is employed as a general antiseptic.

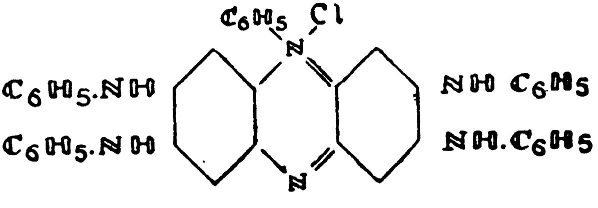
The *Azines*, which have the typical grouping,



constitute another important family. Mauve, the first of the synthetic dyes, is interesting historically but is little used, except to a limited extent for paper printing and shading bleached silk. Other typical dyes of this family are the *Safranines*, *Indulines*, *Nigrosines* and *Aniline black*. The safranines, the simplest of which (phenosafranine) has the formula,



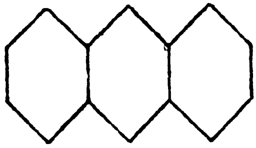
are beautiful red, violet and blue dyes. They dye wool, silk and cotton, but the latter must first be mordanted. One of the safranines is used for staining microscopic preparations. The indulines comprise blue, violet, and black dyestuffs. *Fast blue R*



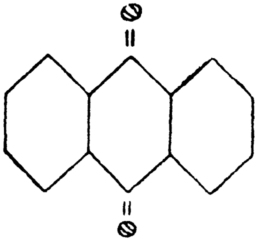
is made by heating a mixture of aniline, hydrochloric acid and aminoazobenzene, the latter also being obtained from aniline. The indulines are insoluble in water, but soluble in spirit; they are used to colour varnishes and shoe polishes, and for making inks. They can be made soluble in water with sulphuric acid, and then become fast blues for wool, silk and mordanted cotton.

The exact molecular architecture of the nigrosines is still unknown. They are made by heating a mixture of aniline, hydrochloric acid and nitrobenzene. The resulting product is insoluble in water, but soluble in spirit; it can be made water-soluble by treatment with sulphuric acid. The nigrosines are mainly employed for shoe-blacking, stove polish and for colouring leather and varnishes.

A very important family of dyestuffs is derived from the hydrocarbon anthracene; this is the *Anthraquinone* family. Anthraquinone is just anthracene with two of its hydrogen atoms replaced by oxygen.

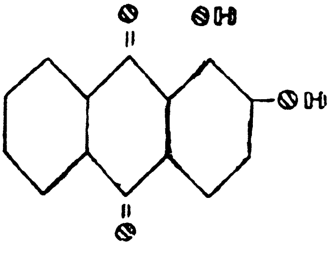


anthracene



anthraquinone

If we heat anthraquinone with sulphuric acid we get a sulphonic acid, the sodium salt of which, when fused with caustic soda and treated with acid, yields the dye *Alizarin*—



This is the principal colouring matter of the madder root. Although it has taken you less than five seconds to read about the preparation of alizarin it took twenty years to find it out. Two French chemists, Robiquet and Colin, extracted alizarin from the madder root in 1828, but it was not until forty years later that Graebe and Liebermann found that the dyestuff was a derivative of anthracene. Although they managed to synthesise minute quantities of the substance—not, however, by the method described above—the process was too dear to compete with the natural product. Then followed a race between Perkin in England and Graebe and Liebermann in Germany to see who could devise a cheap process for making alizarin from anthracene. The German chemists won by a day! They filed their application for a patent on June 25th, 1869; Perkin filed his application on June 26th. This was the first of the natural dyes to be synthesised. The year 1869 marked a turning point in the dye industry. At that time, 50,000 acres were devoted to the cultivation of madder, the annual output of which was 750 tons. Yet in 1875 not an acre of ground in Europe was producing the dye; it had been completely replaced by the synthetic product. Within ten years the price dropped from £50 per ton to £18.

Madder has always been an important dye throughout the ages. Like indigo, it was cultivated in Egypt and India over five thousand years ago. Its value as a dye depends upon its ability to unite with certain metallic oxides (mordants) to form insoluble, brightly coloured lakes that are very fast to light, and by varying the oxide we can get different shades of violet, claret, blue and red. The famous Turkey red is made by using aluminium oxide.

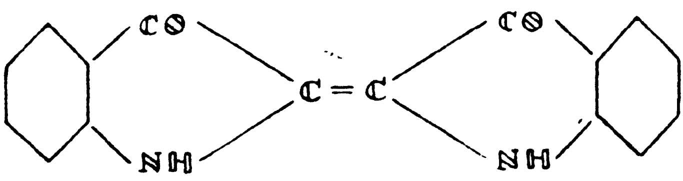
A group of dyes known as the *Purpurins* are present with alizarin in the madder root, but they are now manufactured by the oxidation of alizarin. *Purpurin* itself gives scarlet shades; *Flavopurpurin* gives yellowish-red shades with aluminium, and violet-red with iron mordants.

A group of dyes belonging to the anthraquinone family, known as the *Indanthrenes,* was discovered in 1901. The first of these was *Indanthrene Blue RS.* The indanthrenes are vat dyes, that is they are pigments insoluble in water, but yield solutions of colourless or nearly colourless compounds with certain alkaline substances. These compounds are absorbed by the fabric, which is dipped into the solution, and are converted back to the coloured pigments by exposure to the air. The dyes are thus firmly fixed in the fibres. Indigo is a typical vat dye, although it differs chemically from the indanthrenes.

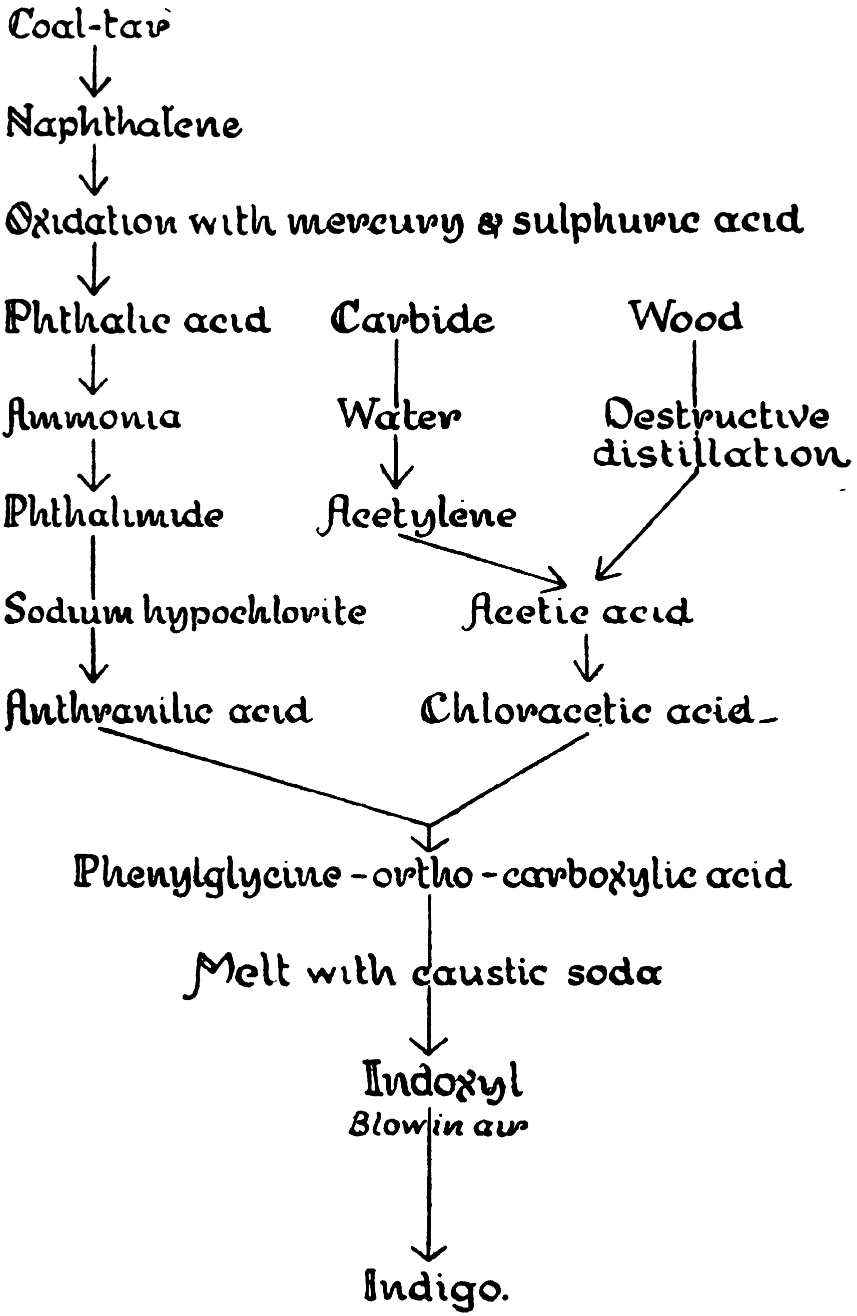
Indigo is the most important member of the indigoid family of dyestuffs. Its history is full of romance. It was described in the old Sanskrit writings of India; it was extracted by the Hindus and converted into a soluble form for dyeing. Then the

Egyptians learnt of its use and employed it not only to dye the clothes of the living, but also of the dead; mummy wrappings five thousand years old have been found to be dyed with indigo. Pliny tells us of its introduction into Greece and Rome; of the beautiful purple flame it gives when heated; and of the attempts to imitate it. According to Thorpe and Ingold the Romans appear to have used indigo not as a dye, but as a kind of paint; this means that they did not get it into solution before applying it to fabrics. It was introduced into Europe in 1516, but as the use of woad was well established at this time the woad cultivators attempted to keep it out by spreading false accounts of its properties. It was said to soil fabrics, and many laws were passed forbidding its use under dire penalties. Since the English laws on this point have never been repealed, it is still illegal to wear an indigo-blue serge suit!

Somewhere about 1850, several chemists examined indigo and concluded that its molecule contains 16 carbon atoms, 10 hydrogen atoms, 2 oxygen atoms and 2 nitrogen atoms. Its formula is hence $C_{16}H_{10}N_2O_2$. As far back as 1826 Unverdorben had distilled indigo and obtained aniline, which incidentally receives its name from the Arabic name for indigo, *anil*. But to reverse the process and get indigo from aniline was another thing. For years chemists tried to find out how the atoms are arranged within the indigo molecule; they knew that the determination of its structure was a prelude to its synthesis. The great German chemist, Adolph von Baeyer, who died at Munich in 1917, not only determined its structure, but also synthesised it by several different methods. Indigo is



and with the help of this formula no fewer than five different methods have been devised for synthesising the dye from benzene, toluene and naphthalene. Baeyer first synthesised


Coal-tar
Naphthalene
Oxidation with mercury & sulphuric acid
Phthalic acid
Ammonia
Phthalimide
Sodium hypochlorite
Anthranilic acid
Carbide
Water
Acetylene
Wood
Destructive distillation
Acetic acid
Chloracetic acid
Phenylglycine-ortho-carboxylic acid
Melt with caustic soda
Indoxyl
Blow in air
Indigo.

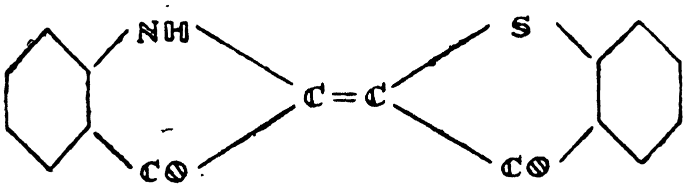
MANUFACTURE OF ARTIFICIAL INDIGO

FIG. 41

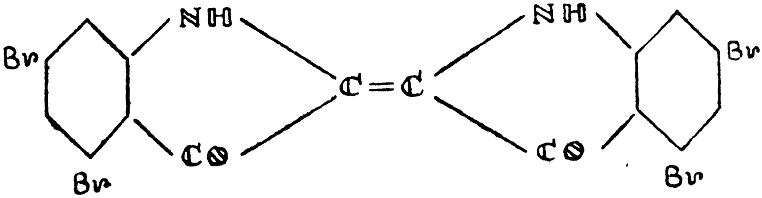
the dye in 1880. Seventeen years elapsed, however, and about £1,000,000 was spent before it could be produced on a commercial scale by the Badische Anilin und Soda Fabrik, the big German dye firm. In 1897 nearly a million acres were devoted to the cultivation of the indigo plant, the annual value of the crop being £4,000,000. Since that date the natural product has gradually been driven from the market by the cheaper synthetic product, which is just the same chemically but purer and more reliable. A hundred years ago indigo cost nearly £1 per lb.; in 1914 when prices were at their lowest it could be purchased for less than a twentieth of this price from Germany, who was then *selling*—not consuming—£2,500,000 worth of the dye per annum.

Artificial indigo is now made from naphthalene, which is first converted into a substance known as phthalic acid by means of sulphuric acid. Normally the action is too slow to be of any practical value, but one day, so the story goes, an assistant broke a thermometer bulb in a hot mixture of sulphuric acid and naphthalene, with the result that phthalic acid was rapidly formed; the mercury in the thermometer had acted as a catalyst. Some careless laboratory assistant therefore laid the foundation of the synthetic indigo industry. Without him perhaps another £1,000,000 would have been spent in finding a commercially successful process. The phthalic acid is then taken through a series of reactions resulting in indigo (p. 291).

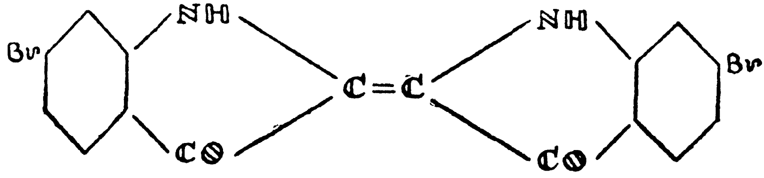
Subsequent developments have proved as interesting as the original indigo synthesis. Until 1906 the indigoid family was only represented by indigo. In that year Friedländer discovered that a violet dye could be made by introducing one sulphur atom into indigo in place of a nitrogen and hydrogen atom. It is known as *Ciba violet*—



Introduction of another sulphur atom yields another dye, *Thio-indigo red,* and by reshuffling the atoms in the indigo molecule yet another dye named *Indirubine* can be formed. Again, if bromine atoms are put in place of some of the hydrogen atoms in the indigo molecule we get reddish-blue dyes such as *Ciba blue 2B*—



In 1909 Friedländer made a very interesting discovery concerning Tyrian purple. Strangely enough this dye had been synthesised and put on the market in 1904, but in complete ignorance that it corresponded to the purple of the ancients. Friedländer extracted the colouring matter from 12,000 of the molluscs and analysed it. He found it to be dibrom-indigo—



That is, indigo with two of its hydrogen atoms replaced by two bromine atoms.

Not only are the indigo dyes used for dyeing fabrics; they are used to colour our food and confectionery. Sweets, drinks, ices and cakes look more attractive when coloured and, provided the dyes are not harmful, there is no objection to their use for this purpose. Among the more important food dyes are indigo; *Naphthol yellow S* and *Erythrosine,* which are both made from naphthalene; and *Ponceau 3R.*

After the introduction of acetate artificial silk, it was found that it did not dye well with the existing dyestuffs, and consequently a special series had to be invented for the purpose. The first of these, the *Ionamines*, are insoluble azo and anthraquinone dyes, made temporarily soluble by introducing into their molecules certain groups of atoms. Once the soluble dye has been applied to the acetate silk, these groups are split off and leave the insoluble dye in the fibre. The S.R.A. colours are insoluble azo-dyes suspended in a finely divided state in castor oil dissolved in sulphuric acid; anthraquinone dyes similarly treated form the *Duranol* series. These dyes will not colour cotton, linen, or any of the other forms of artificial silk (Chardonnet, cuprammonium and viscose), and hence they can be employed with other dyes for producing multicoloured effects on fabrics woven from acetate silk and other forms of artificial silk, or any of the natural fibres.

Dyestuffs serve other purposes besides dyeing. Some are powerful disinfectants and antiseptics, and are used with success in medicine for destroying the bacteria responsible for certain diseases. *Trypan red* and *Trypan blue,* two azo-dyes, are employed for this purpose. *Acriflavine,* a yellow dye as its name implies, is used for treating wounds. It is highly antiseptic and, unlike carbolic acid and other antiseptics, stimulates rather than inhibits the process of healing. *Methyl violet, Eosin*—a dye whose lead compound forms the bright red pigment used for poster printing—and a dye known as *Methylene blue,* have been administered internally for various complaints. The latter is a constituent of some patent medicines for curing rheumatism and diseases of the kidney.

Coal-tar dyes are further employed for photographic purposes in order to make sensitised plates and films more sensitive to light of a certain colour. The emulsion on photographic plates is most susceptible to the blue and violet rays, but by treating it with suitable dyes it can be made equally sensitive to the other colours of the spectrum, viz. red, green and yellow. Plates so treated are said to be panchromatic. In addition special dyes can make plates sensitive to yellow and green rays; they are then called orthochromatic. The dyes eosin and erythrosin and a special group known as the *Pina* dyes—*Pinaverdol*, *Pinachrome* and *Pinacyanol*—find important application in photography.

Coal-tar colours are used in infinitesimal amounts by biologists and pathologists for staining specimens for microscopic work. Thus bacteria, nerve endings and fatty tissue can be readily recognised by their ability to take up special dyes. Methylene blue, eosin, malachite green and Sudan III are employed for this purpose. It was by using methylene blue as a stain that Koch discovered the bacillus of cholera and tuberculosis. In this connection it is interesting to note that the employment of dyes as microscopic stains led to the discovery of a new class of dyestuffs. In 1886 Ehrlich observed that methylene blue stained living nerve tissue and he attributed this to the presence of sulphur in the molecule. In order to verify this, he asked Caro to make a dye like methylene blue with the sulphur replaced by oxygen. Caro obliged, and discovered a new series of dyes—the *Rhodamine* colours.

The dye industry, which is intimately associated with the textile, explosive, agricultural, leather, rubber, printing, perfume and food industries, is responsible directly or indirectly for the employment of millions of people. Before the war, Baeyer & Co., the big German dye firm, employed 10,000 men, upon whom were dependent 15,000 women and children. Included in the employees were 330 university trained chemists and 10 doctors. Although the synthetic dye industry had its origin in England, in 1914 we were importing dyes to the value of £2,000,000 from Germany—dyes essential for the manufacture of £200,000,000 worth of goods produced by 1,500,000 workers. The dye industry in this country experienced a steady decline from 1880 onwards when Germany carried off a large part of the business. In the 'seventies the Badische Anilin und Soda Fabrik Co. began to make dyes and with other firms established a flourishing dye industry in Germany. In that country the organic chemical industry, the mainspring of which was dyes, developed in an amazing fashion as a result of the combined efforts of the Government, banks, industrialists and trained chemists. Before the war Germany manufactured more than three-quarters of the coal-tar products of the world. The British Government altered Perkin's name to Sir William, but paid no heed to his requests for help to develop the dye industry on sound lines in this country. In 1874 he retired from the dye business, blighted by the keen and merciless competition from Germany. He pointed out that the classical education of our universities trained the youth of the nation to be gentlemen, not chemists. The blame, however, should not have fallen on the universities entirely, for when they did train some of their students as chemists the British manufacturers refused to employ them, preferring to keep to the rule of thumb methods of their forefathers. Conservatism has been the bugbear of British industry in the past. Until comparatively recently, our manufacturers have been indifferent to the scientific control of their processes and to the practice of research, which is essential for the development of any industry. This basic fact was soon recognised in Germany, where the dye factories became the training ground of research chemists, who were recruited from the universities. The position of the chemist in industry was fully appreciated by both the German universities and industrialists. In the last fourteen years of the nineteenth century over 1,000 dye patents—the results of intensive research—were filed by German investigators, but there were only 86 British. It is not that German research is superior to British research. Both nations have made equally important contributions towards the development of chemistry, but English industrialists never have taken the long view and encouraged research. We cannot blame the Germans if they seized the opportunity that we let pass. The favourable position they occupied in the chemical industry was, in a measure, due to their carrying out of the chemists' commandment to the very letter: *Thou shalt not waste.* Careful attention was given to the recovery of by-products and their conversion into useful chemicals or commodities.

Even in 1885 only 20 per cent of the dyestuffs used in this country were home produced, and this in spite of the fact that we were then leading the world in textiles, which are not saleable unless dyed. In 1914, after the outbreak of war, not only was our textile industry crippled through lack of dyes, but our armies in the field were short of medicines and drugs; these had previously been imported from Germany. It was only the European conflict that brought home to our manufacturers and industrialists the danger of relying upon another country for coal-tar products. Steps were then taken to revive the British dye industry, which for a few years enjoyed unprecedented prosperity. German patents were revoked and first-class chemists, experienced in technical dyestuff research, were employed in the factories. Messrs. Levinstein Ltd. and Read, Holliday—one of the earliest English synthetic dye firms—increased their output at the beginning of the war. The latter were bought out in 1915 by the British Dyes Ltd., with the financial assistance of the Government, and three years later this firm amalgamated with Messrs. Levinstein as the British Dyestuffs Corporation Ltd. At that time the output in this country amounted to 13,600 tons, the highest figure ever reached. In 1920 a trade slump fell on the country and the dyestuffs industry was the first to suffer. Its condition was aggravated by over-production, severe competition resulting from the return of the German market, the importation of German dyes on account of reparations, and the rapid depreciation of the mark. The result was that in 1920 we were importing £7,500,000 worth of dyes from Germany, the Sankey judgment having declared illegal the Order in Council prohibiting the importation of foreign dyes. In the hope of preventing the complete collapse of the dye industry in this country the Dyestuffs Import Regulations Act was passed in December, 1921, forbidding the importation of dyestuffs and intermediates except under special licence. Licences are granted if the commodity required is not manufactured here or if the home price is prohibitive; if the home price is more than twice the foreign, the buyer can go abroad. In spite of this Act, the German dye output is about five times that of this country.

German manufacturers made an effort to regain their trade by internal co-operation, leading to the formation in 1925 of the Interessen Gemeinschaft Teerfarben Industrie A.G.—the well-known " I.G."—which embraced the six largest dye firms. The combined capital ran into 1,100,000,000 marks. By this amalgamation economy of manufacture was ensured, the new knowledge resulting from research was pooled, and the overlapping of processes avoided. As a result the German dye output is about 85 per cent of the pre-war figure. The German amalgamation was followed in this country in 1926 by the formation of the Imperial Chemical Industries Ltd.; this resulted from the merging of Brunner Mond and Co. Ltd., Nobel Industries Ltd., The United Alkali Co., and British Dyestuffs Corporation Ltd.

CHAPTER XII

HARNESSING MICRO-ORGANISMS

It is commonly supposed that micro-organisms are a peculiar race of living things, always lying in wait to strike man down with some deadly scourge. This belief had its origin in the discovery, made some seventy years ago, that many diseases are associated with the activity of a few particularly virulent bacteria. To assert therefore that all bacteria should be shunned by man is patently absurd. These organisms play a very important part in health, disease and industry. It is true that some bacteria are our worst enemies. On the other hand there are some that are not only perfectly harmless, but must be included among our best friends. Relatively few of us realise the important position bacteria occupy in the web of life. Indeed, it would not be exaggerating to assert that our very existence and that of every living thing, depend upon their activity. All living beings derive their nourishment directly or indirectly from the soil, the fertility of which is maintained by the bacteria present in it. In the chemical sense there is no such thing as Death; it is merely an atomic rearrangement. When an animal or plant dies the chemical substances present in the tissues are resolved by the bacteria of putrefaction, always present in the air and the soil, into simpler bodies, which are broken down further by other bacteria into chemical compounds that can be utilised by plants for their nourishment. Living matter springs from the soil and eventually returns to it. Soil bacteria are the connecting link between Life and Death. They are the agents responsible for the eternal circulation of matter. The Greek philosopher, Heraclitus, knew nothing about bacteria but he realised that incessant change is going on in nature:

> Change is everywhere; everything is and is not. Even in the same river one cannot bathe twice, nor even once.

And Shakespeare puts the following words into the mouth of Hamlet:

Imperious Cæsar, dead and turned to clay,
Might stop a hole to keep the wind away:
O! that that earth, which kept the world in awe,
Should patch a wall to expel the winter's flaw.

It is interesting to note that a recent novel is based on the assumption that a new kind of bacteria suddenly arises and kills all the useful soil bacteria. A famine results and millions die of starvation.

Bacteria are the smallest living things known—a quarter of a million of them could quite easily be covered by the full-stop at the end of this sentence—and for this reason they are sometimes called micro-organisms. Many jokes were made about them when their existence was first brought to the notice of the public. As one book said: " In Germany they were called germs, in France parasites, and in Ireland microbes." Some of them are beyond the range of our most powerful microscopes. Although we cannot see them we can observe their effects because with other lowly forms of life, such as the moulds and yeast cells, they are the agents of fermentation. Fermentation is one of the most wonderful chemical processes going on around us. It is a decomposition or transformation of complex organic matter into substances of simpler composition by the vital activity of micro-organisms. In its widest sense fermentation embraces the chemical processes of life. Every living cell, whether it be that of an elephant or a bacterium, contains a jelly-like mass called *protoplasm*, which Huxley defined as " the physical basis of life ", and this protoplasm is provided with a special mechanism for breaking down and building up complex organic bodies. The protoplasm is the seat of the constructive and destructive chemical processes that go on within all living cells. It is true that in common parlance fermentation is usually associated with *alcoholic fermentation*, that is the production of alcohol from the decomposition of sugary liquids by means of the cells of the yeast plant. Indeed, this meaning was attached to the word as late as the middle of last century. We must bear in mind, however, that fermentation is a process set up by living cells.

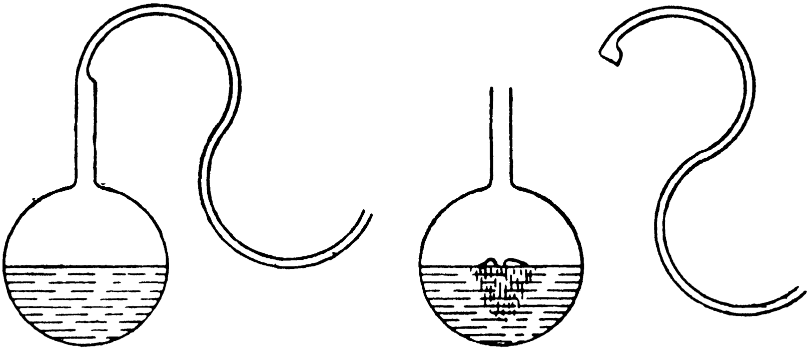
To return to bacteria. They are unicellular; that is, each organism consists of a single cell. By the use of special stains it can be shown that the minute blob of protoplasm constituting the cell is surrounded by a cell wall. Like all living things they have the power of reproduction and they propagate by splitting across the middle, each half forming a new cell. For reasons that are not profitable to discuss here bacteria are regarded as the lowest members of the plant world. They are members of the group which botanists call *fungi*, which includes yeast and the moulds that grow on jam, cheese, damp bread and old boots. Fungi differ in two remarkable respects from other plants; they do not possess the green colouring matter, chlorophyll, characteristic of all green plants, nor can they use the carbon dioxide of the air as a source of carbon to build up their tissues. Whether they possess no chlorophyll because they cannot use carbon dioxide, or cannot use carbon dioxide because they possess no chlorophyll, is a question we cannot answer. It is another variation of whether the hen or the egg came first. The chlorophyll of green plants enables them to absorb the energy of sunlight, and by means of this they are able to build up the proteins and carbohydrates from the carbon dioxide of the air and from the salts and water present in the soil. Bacteria and fungi, being denied the energy of sunlight and hence the synthetic power of the green plant, must obtain the energy required to maintain life from some other source. All living things require a supply of energy—the driving force of all vital phenomena. Life manifests itself by the taking in of energy in one or more forms and the giving up of it in others. *All living cells are in fact energy transformers.* Where does the energy required to maintain the life of bacteria and fungi come from? The answer is supplied in the word fermentation. These micro-organisms break down the organic matter on which they feed into comparatively simple substances, and this chemical decomposition is accompanied by the liberation of a large amount of energy. This process is fermentation. Fermentation is thus a means employed by lowly organisms for obtaining energy.

Green plants obtain their energy from the sun. Human beings and animals obtain theirs by the oxidation or burning up of foodstuffs within the living cells. Chemical energy is liberated by the action of the oxygen of the air on the carbon and hydrogen of the foodstuffs, and this energy can be transformed into other forms, e.g. heat and mechanical energy. Bacteria and the fungi get their energy by breaking down, that is fermenting, complicated organic substances. We cannot do better than quote the words of Hoppe-Seyler, one of the most famous of nineteenth century bio-chemists:

> In all fermentation heat and energy are liberated; a large class of lower organisms, including yeast, live by this process. They do not draw their energy from the light and heat of the sun like green plants, nor as animals do from the affinity of oxygen for other elements, but from the relatively limited power indicated (i.e. fermentation), by which complicated organic substances are resolved into simpler ones.

The development of microbiology—the study of bacteria and microscopic forms of life—runs parallel with the development of the microscope, which was first invented in 1590 by Janssen, a Dutch spectacle maker. Towards the end of the next century another Dutchman, Antony van Leeuwenhoek, amused himself by making microscopes and examining all kinds of objects beneath them. In 1675 he examined a drop of dirty water and saw a number of little specks, an account of which he gave in a letter to a friend. These were undoubtedly bacteria. Six years later he discovered bacteria in saliva and sent an account of his discovery to the Royal Society in London. Leeuwenhoek did not call these micro-organisms bacteria, but animalcules, a name that was retained for nearly two centuries. It is interesting to note that in the middle of the next century a Viennese doctor, named Plenciz, propounded a theory of infectious disease, associating a special micro-organism with each disease. This idea reappeared a century later and was forcibly demonstrated by Pasteur and Koch, who laid the foundations of the germ theory of disease.

From the time of Aristotle (died 322 B.C.) until the nineteenth century the idea prevailed that living creatures could be engendered from dead matter, in other words they could be spontaneously generated. After the discovery of micro-organisms it was asserted that they were spontaneously produced from decaying matter. Several attempts were made to disprove this view, but no really conclusive evidence was obtained until 1860, when Pasteur, in a masterly piece of research, proved that micro-organisms had their origin in the air. He took a number of flasks containing liquids subject to rapid putrefaction, such as broth and milk, and drew out the necks of the flasks in the form of a letter " S " on its side (Fig. 42).



PASTEUR'S FLASKS.

FIG. 42

This experiment proved that fermentation and putrefaction are caused by micro-organisms present in the air, and that micro-organisms are not spontaneously generated from dead matter. The S-shaped flask on the left contains a putrescible or fermentable liquid (meat broth, milk) which is boiled for a considerable period to destroy any micro-organisms initially present. The flask is left, with the mouth open, for days—or even months or years for that matter—without any sign of putrefaction. This is because the S-shaped bend allows air to get in, but any solid matter or micro-organisms are trapped on the floor of the bend and stop there. But if the neck is severed, as in the figure on the right, so that organisms can fall from the air directly into the liquid, putrefaction rapidly sets in. Examination of the liquid under the microscope shows that it is teeming with rapidly multiplying micro-organisms.

He then boiled the contents of the flasks for a long time to kill any micro-organisms initially present. The flasks were allowed to cool and left in the still air of a room with the mouths open. Months elapsed without putrefaction setting in, although the flasks were open to the air. The " S " shaped bend trapped any solid matter present in the air and prevented it from getting to the liquid in the flasks. But once the necks of the flasks were severed, so that solid matter could settle from the air on the surface of the liquid, putrefaction soon commenced. Pasteur observed the formation of a scum in all the flasks with the severed necks, and a microscopical examination of the contents showed that they were teeming with rapidly multiplying micro-organisms. Pasteur drew two conclusions: that fermentation and putrefaction result from the action of air-borne organisms; that micro-organisms are not spontaneously generated from lifeless matter, but have their origin in the air—they are derived from pre-existing living organisms floating about around us. All biologists now believe that living things can only be derived from pre-existing living things.

The story of fermentation is one of the most fascinating in the history of bio-chemistry. We must remember, of course, that until the end of the eighteenth century the term fermentation was synonymous with alcoholic fermentation, and as such has always made a strong appeal to the mind of both layman and savant throughout the ages. The names of some of the most illustrious chemists are to be found inscribed on the roll of those who have investigated this highly important branch of bio-chemistry. The interest that alcoholic fermentation has always had for the scientific mind is certainly not only due to the fact that one of its products is alcohol, but rather because it exhibits, in the words of the immortal Lavoisier, "one of the most striking and extraordinary reactions presented by chemistry". The researches of those who have investigated this absorbing subject have had a most widespread influence; they have opened up new horizons in many fields of chemistry and general biology.

Acquaintance with fermented plant juices must have been coeval with the earliest stages in the development of the human race. It is extremely probable that the discovery of the change of sweet grape juice into wine was purely accidental, having arisen from observations on crushed grapes that had been allowed to stand for some time. Similarly the preparation of mead can be traced to the accidental fermentation of honey. At an early stage in his civilisation man considered that fermented drinks were produced by some mysterious, if not divine, agency. He could not fail to note the more obvious phenomena of alcoholic fermentation; the gradual rising of the grape or other fruit juice with the evolution of gas and the formation of a thick froth on the surface of the liquid; the change of odour and taste from the sweet to the spirituous, and finally to the acid and fetid. We know that the gas is carbon dioxide, which is in fact responsible for the exhilarating and pleasant properties of fermented liquids, and that the spirituous taste and smell are due to the production of alcohol in the liquid. Our primitive ancestors also noted the ease with which fermented liquids began to putrefy, and so at a very early date the two processes, fermentation and putrefaction, were closely associated. As a matter of fact they *are* very closely associated. They both result from the activity of micro-organisms living on organic matter, which they decompose to get energy.

Much that appears novel to the reader was known to the ancient peoples. Yeast was known to the Jews and Egyptians, who undoubtedly appreciated the fact that a small quantity of it could ferment sweet liquids and raise unleavened dough. They knew that leaven could be made by inoculating dough with yeast, which they supposed was either spontaneously generated by some occult force, or was derived from pre-existing yeast from time immemorial. Fundamentally considered, the latter view was not far from the truth. The idea that fermentation is a process akin to life is by no means modern. It appears in the Bible, in the Vedas, the sacred books of the Hindus, and is still met with among the less civilised tribes. Even to-day the Mohammedans of the Caucasus attribute to the intervention of Allah the production of kephir grains, which are used in the preparation of koumiss or fermented mare's milk.

This association between fermentation and life echoes down the centuries. We meet it again in the Middle Ages with the alchemists. But they rather confused the frothing occurring in alcoholic fermentation with the giving off of gas in ordinary chemical reactions, e.g. when soda dissolves in vinegar or lemon juice. Consequently the word fermentation gradually became synonymous with any sort of frothing or bubbling. The foundations of our chemical knowledge of alcoholic fermentation were laid towards the end of the eighteenth century by Lavoisier (1743–1794), who showed that during the process sugar is split up into approximately equal parts of carbon dioxide and alcohol. In the early part of the nineteenth century, chemistry began to make rapid strides and after the synthesis of organic compounds by such able chemists as Wöhler and Liebig, vitalism fell into disrepute. A few biologists tentatively suggested that some connection existed between the activity of micro-organisms and the processes of putrefaction and fermentation, but their views were completely overshadowed by those of Liebig, the great German chemist whose name is commemorated in condensers and meat extract. Liebig's theory, which will be comprehended if the reader refers back to the chapter on explosives (p. 210), is briefly this: In all types of fermentation a ferment (e.g. yeast) is necessary and is formed from fermentable matter by the action of atmospheric oxygen. The molecules of both ferments and fermentable substances (e.g. sugar) are particularly unstable—like a house of cards ready to fall down at the slightest touch—similar in fact to the molecules of detonators, only differing from them in not being explosive. The unstable ferment molecules break down under the influence of the oxygen of the air, and the molecular disturbance passes on to the neighbouring molecules of the fermentable matter. The disturbance passes from molecule to molecule, as it does when an explosive is set off by a detonator, and so through the whole mass. This disturbance, said Liebig, is fermentation. Ingenious as this theory was it took no account of certain facts revealed by the microscope. In 1680 Leeuwenhoek, the Dutchman who discovered bacteria, examined yeast under the microscope and saw that it consisted of "oval globules of pellucid material", but he did not consider it living. His observations attracted little attention until 1835, when Cagniard de Latour, a very versatile French scientist, pointed out that these oval globules are not only living but are the cause of fermentation. Kützing and Schwann in Germany also regarded fermentation as a physiological process associated with the activity of yeast cells and other micro-organisms. Despite the brilliant achievements of these and other investigators their views somehow seemed to have missed fire, and were passed over by contemporary chemists who, we must regretfully add, slavishly upheld the theory expounded by Liebig. Since he occupied a unique position of authority in the chemical world his views were generally accepted. The facts of the biologists were denied by the chemists, who this time were in the wrong. Liebig was hardly able to conceal his contempt for the theory that fermentation is caused by the physiological activity of such insignificant creatures as micro-organisms. In his opinion the theory was only worthy of comparison "with the idea entertained by a child, who explains the rapid current of the Rhine through the numerous Rhine mills at Mayence by supposing that the mill-wheels, by their force, urge the water downward toward Bingen".

An authority on both biology and chemistry was required to clear the air. This was accomplished by Louis Pasteur. The distinguishing feature of his work was not so much that he discovered facts, although perhaps he extended our knowledge on fermentation more than any other investigator, as that he repeated and perfected the experimental methods of his predecessors. Pasteur opened the eyes of the world to the importance of the microscopic beings that inhabit the earth. He proved that they can grow and multiply on mineral matter plus the simplest of carbon compounds, such as sugar or starch, and that they can obtain the nitrogen necessary for building up proteins from nitrates and ammonium compounds. Pasteur's investigations on fermentation, commenced in 1857, extended over a period of twenty-two years. So far-reaching have been their results that their importance cannot be estimated. They definitely proved fermentation to be correlated with the life of special micro-organisms that multiply with incredible velocity; they revolutionised the brewing industry and the theory and practice of medicine in so far as it is concerned with infectious disease; and they heralded the approach of antiseptic surgery.

When Pasteur began the study of fermentation he admitted that the idea of living matter causing fermentation was a preconceived one. This illustrates the importance of an *idea* in scientific research. Mixing substances indiscriminately in test-tubes or distilling them at random rarely produces results. An idea or hypothesis is needed to guide the investigator. When Leonardo da Vinci—that most versatile Italian of the fifteenth century—said, "hypothesis is the general and experiments are the soldiers", he probably meant that an idea directs or indicates what experiments should be made. In 1857 Pasteur was investigating the action of certain moulds on the two forms of tartaric acid, and he discovered that a mould called *Penicillium glaucum* feeds on and ferments one form—dextro-tartaric acid—but leaves unchanged the other form, known as laevo-tartaric acid. This discovery in itself strongly hinted at a connection between the decomposition of organic substances (i.e. fermentation) and microscopic life. Within the next few years Pasteur proved without a shadow of a doubt that the alcoholic fermentation of sugar, the formation of lactic acid in the souring of milk, the transformation of alcoholic liquids into vinegar, and the putrefaction of organic matter are caused by specific micro-organisms. Pasteur proved that a specific fermentation is brought about by a specific organism. He showed that when milk sours, a certain micro-organism converts the sugar present in the milk into lactic acid, and that under certain conditions another organism develops, transforming the lactic acid into another substance, butyric acid. This is present combined with glycerin in butter-fat. But unlike the other micro-organisms that he had studied Pasteur found that the one producing butyric acid in milk grew and fermented in the complete absence of air; indeed, it would neither develop nor cause fermentation if air were present. Pasteur soon discovered that the organisms associated with putrefaction behaved in the same way, and he was also led to recognise that yeast and moulds could live both with and without air. With a free supply of air their growth was more vigorous but their power of bringing about fermentation was diminished; without air growth was not so vigorous but the ability to cause fermentation was increased. These observations formed the basis of a novel theory: *Fermentation is life without air.*

Pasteur's theory is simply this: All organisms and in fact every living organ and cell need oxygen. If they can obtain it from the air they do so, but their power of causing fermentation is very limited. Deprive them of *free* oxygen, and they will obtain this element from substances containing it in the *combined* state. The organisms then become ferments, abstracting oxygen from compounds containing it. This, in effect, is fermentation. The decomposition of substances rich in oxygen is accompanied by the liberation of heat and energy, which are utilised by the fermentation organism. In the words of Pasteur:

> The character of a "ferment" (ability to cause fermentation) is inherent in all living cells and there are as many types of fermentation as there are of different micro-organisms. Fermentation is, therefore, a very general phenomenon, caused by the growth and multiplication of micro-organisms out of contact with free oxygen,

under which circumstances they acquire the power of abstracting oxygen from chemical compounds in the medium in which they are growing. The heat and energy required by the organisms to effect their movement, growth and reproduction results from the decomposition of fermentable matter, which like an explosive, liberates heat on decomposition.

Although Pasteur's views have been generally accepted for many years, the doctrine: *Fermentation is life without air*, has been the subject of much controversy. At the beginning of the present century it was generally discredited. Within the last twenty years, however, evidence has gradually accumulated from different sources in favour of its general truth.

If micro-organisms cause fermentation and putrefaction, where do they come from? Why do substances appear to ferment and putrefy spontaneously even in the absence of fermentable and putrescent matter? Pasteur proved that the spores or germs of micro-organisms are floating about in the air. When these spores alight on food or sugary material they develop into adult organisms, which propagate freely and so cause fermentation. Pasteur isolated the germs of several bacteria by filtering air through gun-cotton, which he afterwards dissolved away with a mixture of alcohol and ether. He showed that the germs of yeast cells causing grape-juice to ferment are present in the air and on the skins of the grapes. Similarly, the spores of the micro-organisms of putrefaction are floating about in the air and when they settle on such food as meat or fish, they readily set up putrefaction, which is really a type of fermentation. In principle there is no difference between meat going bad and grape-juice turning into wine; both changes are brought about by micro-organisms. Pasteur proved that fermentable or putrescible matter could be kept fresh indefinitely, even in contact with air, provided the latter be germ-free or sterilised. He showed that sterilisation can be effected by heating the putrescible matter to the temperature of boiling water for several hours. Preservation of food by heating is still known as pasteurisation.

From his studies of the diseases of beer Pasteur realised that they were caused by harmful bacteria settling in the liquid after the brewing operations. This led him to regard epidemic disease as the outcome of the failure of plant and animal life to resist the attacks of the inimical forms of micro-organisms and their spores present in the dust of the air, in soil and water, and even on food. He threw a flood of light on the origin of infectious disease. Sir William Osler writes:

> At the middle of the last century we did not know much more of the actual causes of the great scourges of the race, the plagues, the fevers, and the pestilences, than did the Greeks. Here comes in Pasteur's great work. Before him Egyptian darkness; with his advent a light that brightens more and more as the years give us ever fuller knowledge.

Pasteur laid the foundations of *serum-therapy* in 1880 when he showed that anthrax bacilli, kept at 42° C. in chicken broth, lose their virulence in a short time and are not then fatal even to mice. Like so many discoveries this arose from an accident, or even possibly from carelessness on the part of Pasteur. The incubator used for the bacilli should have been kept at 37° C., but either through an oversight or a faulty temperature control the temperature went up to 42° C., with the result that the bacilli became attenuated or less virulent. Animals inoculated with a preparation made from these bacilli resisted the deadly effects resulting from inoculation with the normal anthrax bacilli; in other words they had immunity conferred upon them. Thus was the principle of vaccination established.

Pasteur observed the similarity between fermentation and the changes occurring in infected wounds. While he was occupied with research on the diseases of wine and beer, Lord Lister in England introduced antiseptic surgery. He realised that the sepsis occurring after surgical operations was due to the infection of the exposed tissues by micro-organisms present in the air, and on the operating instruments. At first he used carbolic to spray the air and sterilise the instruments and wounds. Antiseptic surgery was gradually replaced by aseptic surgery, which is based upon absolute cleanliness; this can be maintained by boiling or heating the instruments, steam sterilisation of dressings and the wearing of sterilised rubber gloves.

Many diseases are produced by parasitic micro-organisms that live on the blood. Blood-poisoning is caused by a pus-forming bacterium that propagates at a rapid rate in the blood, which fortunately resists the organism under normal conditions. Diphtheria, plague, typhoid, tetanus, pneumonia, malaria, hydrophobia, syphilis and tuberculosis are now known to be caused by specific parasitic micro-organisms. In the words of Sir J. A. Thomson: "Nowadays the serpent that bites man's heel is in nine cases out of ten microscopic". W. T. Helmuth livens the situation with a touch of humour:

> Oh, powerful bacillus,
> With what wonder you fill us,
> Every day!
> While medical detectives,
> With powerful objectives,
> Watch your play.

To return to Pasteur's work on fermentation. His dictum, *No fermentation without life*, was strenuously opposed by Liebig and his followers, who saw in fermentation a purely chemical action. In support of this they pointed out that certain fermentation processes occurred in the entire absence of living organisms. It was known in 1833, for example, that a white powder called *diastase* could be separated from barley, and that it possessed the power of converting starch into sugar. At the same time a substance was separated from saliva having the same properties. In 1837 Liebig and Wöhler had discovered that amygdalin, a compound occurring in bitter almonds, could be split up into glucose, benzaldehyde (oil of bitter almonds) and prussic acid by the agency of a non-living body called *emulsin*. Shortly afterwards Schwann, a German biologist, showed that the digestion of protein was due to the action of *pepsin*, a white powdery substance that could be obtained from gastric juice. These changes, which were considered to be examples of fermentation, were clearly brought about by non-living agents. These agents were subsequently called *enzymes*. Enzymes are certainly produced by living plants or animals, but are not themselves living like bacteria or moulds. As a result of these investigations two types of fermentation were distinguished. Fermentation caused by *organised* ferments or by living cells such as bacteria, moulds and yeasts; and fermentation caused by *unorganised* ferments or enzymes, that is by chemically active bodies that can be extracted from the cells of plants and animals and that set up fermentation in the absence of life.

For many years this distinction persisted, although as far back as 1858, when Pasteur was commencing his researches on fermentation, Traube in Germany suggested a novel theory that reconciled the views of Pasteur with those of Liebig. Fermentation, said Traube, is inseparably connected with living organisms, but the act of fermentation is purely chemical. It is brought about by specific ferments (or enzymes as they were later called) secreted by the cells of the organisms, and acting either *inside* or *outside* the cell. Ferments are thus chemical reagents, or catalysts, which initiate and bring about certain definite chemical reactions. Traube's view was generally accepted in 1896 when Buchner showed that in the fermentation of sugar to form alcohol, the active change is not brought about by the direct action of the living yeast cells, but by a substance which he termed *zymase* that is contained in and can be extracted from yeast cells, by crushing them under high pressures. Buchner ground up yeast with sand and subjected the mixture to the enormous pressure of a hydraulic press. The sand tore open the cells, while the high pressure squeezed out a juice that could ferment sugar into alcohol. By adding a mixture of alcohol and ether to the yeast juice Buchner obtained a white precipitate that could be filtered off, dried and powdered. When dissolved in water this white powder still possessed the power of fermenting sugar. Further research has shown that by similar methods enzymes can be extracted from other organisms.

The modern tendency, then, is to ascribe fermentation processes, whether associated with micro-organisms or not, to the activity of the structureless, non-living enzymes, which are themselves produced by living cells. Enzymes are of the utmost importance in nature and industry. They may be looked upon as the "chemical reagents" of the organism. Living cells are minute laboratories in which building up and breaking down processes are going on incessantly. In the human organism food is transformed into bone, flesh and blood, and the contents of the living cells are undergoing a slow combustion to provide heat and energy. In the plant world wonderful syntheses are going on in the cells. Inorganic materials from the air and soil are converted into the organic foodstuffs—proteins, fats and carbohydrates—upon which the very existence of man and the animal world depends. Not only foods but beautiful colouring matters and sweet-smelling essences are made in the plant cells, and although the chemist can make many of them in the laboratory, he has to make use of high temperatures and often high pressures and powerful and corrosive chemicals. In the plant cell the synthesis of even the most complex bodies proceeds quietly at ordinary temperatures because there are present appropriate enzymes to speed up the process. Enzymes also play an important role in digestion. It is largely by their means that the food we eat is made soluble so that it can pass through the wall of the small intestine and be assimilated by the blood.

The harnessing of micro-organisms on an industrial scale is one of the achievements of modern chemistry. The yeast cell has worked for man ever since he cultivated the vine and acquired a knowledge of cereal crops; it is the active agent in the formation of wine and beer. Yeast spores are present on the grapes and in the soil of grape-growing districts. When the grape is crushed the yeast spores develop into mature cells which propagate freely in the grape juice, or "must" as it is called, and bring about the conversion of the grape sugar (glucose) into alcohol and carbon dioxide. After the bubbling due to the escape of the latter has ceased, the "new" wine is drawn into casks which are filled full because air might cause the liquid to sour, with the formation of vinegar. A second fermentation occurs in the casks for several months, the yeast settling to the bottom as lees, while tartaric acid separates out in the form of tartar or potassium tartrate. The clear wine is then allowed to mature for a long time, possibly two or three years, during which time tannin and colouring matters settle out and some of the alcohol combines with small amounts of acids present to form pleasant smelling esters, which are responsible for the bouquet of wine. The wine is finally bottled.

Beer is made by the fermentation of the starch present in cereals, usually barley. Malt is first prepared by steeping barley grains in water and allowing them to germinate or sprout. In this stage the enzyme diastase, which is present in the barley, ferments the starch into maltose, or malt-sugar, and a substance known as dextrin. The malt is then crushed and mixed with hot water and raw grain or potato starch, and the liquid so obtained boiled with hops to impart flavour (*see Plates* 35 and 36). The liquid formed, called beer wort, is now run into fermenting vats and special yeast cultures added, according to the type of beer required. There are many races of yeast and some of them are not suitable for making beer. Until recently the brewer trusted to luck that the yeast he used would make good beer, but now the process is scientifically controlled and special yeast cultures are prepared for brewing by expert micro-biologists. Yeast contains several enzymes and one of them, called *maltase*, converts the malt-sugar into glucose, which in turn is fermented by the enzyme zymase into alcohol, carbon dioxide and small quantities of other substances. Zymase cannot ferment cane sugar. If yeast is added to a solution of cane sugar fermentation does occur, because the yeast cell secretes an enzyme, *invertase*, that converts cane sugar into a mixture of two simpler sugars, glucose and fructose. These are fermentable by zymase.

Yeast finds employment in the baking as well as in the brewing industry. Bakers' yeast is specially compressed. In bread-making the flour—which is largely composed of starch and a protein body called gluten—is mixed with water and a little malt, and some yeast added. On standing in a warm place the yeast acts on the sugar contained in the malt, and the bubbles of carbon dioxide produced inflate the dough and make it rise. At the same time some of the enzymes of the yeast break down the gluten into simpler nitrogenous bodies. The yeast is killed during the baking of the dough and so cannot ferment the bread formed. White bread containing yeast is more nutritious than bread made from a paste of flour and water. This is because yeast contains assimilable fats, proteins, carbohydrates and vitamins, which it abstracts from the organic and inorganic materials present in the liquids it ferments. Owing to its high nutritive value yeast has been used as a cattle food and as the basis of some foods for human consumption, e.g. marmite, which is an extract of yeast similar to meat extract. The superiority claimed for these synthetic yeast products is based upon their high vitamin B content, but since this is most widely distributed in nature it is the most unlikely vitamin to be lacking in an ordinary diet. The high protein content of yeast was realised during the war in Germany, where the rapid growing powers of this micro-organism were utilised for the production of synthetic foodstuffs rich in proteins. "Mineral yeast", a species of *Torula* or bakers' yeast, can grow and synthesise proteins from solutions containing sugars and ammonium compounds, and other organisms can build up foodstuffs rich in fat from the same substances.

Spirits, which normally contain from 40 to 50 per cent of alcohol, are obtained by the distillation of fermented alcoholic liquids. Whisky is made by distilling the "wash" formed by the action of yeast on malted barley, and in addition to alcohol it contains various esters which give it its special flavour. Rum is obtained by fermenting molasses with yeast and distilling the product; it owes its flavour to the esters, ethyl acetate and ethyl butyrate. Brandy is the liquid made by distilling wine.

Apart from its consumption in the form of beverages, alcohol is in great demand industrially. It enters into almost every trade and industry in some form or other. It is extensively used as a solvent in the preparation of varnishes, lacquers and enamel; in the manufacture of anæsthetics such as chloroform and ether; in the making of celluloid, cordite, dyes and collodion; and to a limited extent as a motor fuel (mixed with benzene) and as an illuminant (in conjunction with incandescent mantles). The so-called "solidified" alcohol used for picnic cooking is produced by mixing alcohol and a little ether with collodion. The jelly-like mass formed eventually sets solid and burns away quietly without leaving any residue. Alcohol is used in some countries in heating stoves and in lamps. It is of course obvious that large quantities of alcohol can be made by fermenting sugar with yeast, but sugar is too dear as a raw material. In America crude molasses are used in place of sugar, and in Sweden large quantities of alcohol are made by evaporating and then fermenting the waste liquors from the wood pulp-mills with a special kind of yeast (p. 237). Alcohol is also being produced in America from sawdust and wood-waste, which are mainly cellulose. When cellulose is heated with a little acid and water it is broken down by the latter, or *hydrolysed*, with the production of the sugar, glucose. The wood-waste is hence moistened with acid and heated with steam under pressure. The cellulose in the wood is hydrolysed to glucose, which is then fermented by yeast with the production of alcohol. About 20 gallons of alcohol can be made from a ton of wood-waste. A so-called "new" method has been recently introduced for obtaining alcohol from starchy materials, under the name of the *amylo* process. Actually it has been in use in China and Japan from the earliest times. "Chinese yeast", which has been employed in this process, contains a mould known as *Mucor rouxii*. This is rich in the enzyme diastase and rapidly converts starch into sugar. In France, America and other countries this mould has been substituted by others of the same species. Starchy material (rice, potatoes and maize) is pulped or finely divided and steeped in water, heated in steam to swell the starch granules, and the mash inoculated with the spores of the mould. The mould develops and soon begins to transform the starch into sugar. In twelve to fifteen hours yeast is added, so that the fermentation of starch to sugar by the mould and the fermentation of the sugar to alcohol by the yeast occur simultaneously. In yet another process alcohol can be obtained by the action of certain cellulose-fermenting bacteria on waste vegetable matter, stable manure and sewage.

In all these processes of manufacturing alcohol by fermentation the product never contains more than about 18 per cent and consequently it has to be distilled to produce strong alcohol. It must be remembered that alcohol is a waste product of the yeast cell, just as urea is of the human and animal organisms, and if more than a certain amount of it is formed during fermentation it acts as poison towards the yeast. This does not seem to have been used by temperance reformers as an argument against the consumption of alcoholic beverages. Undoubtedly if taken in large quantities alcohol acts as a poison, dulls the intelligence and becomes habit-forming. There is no evidence, however, that it is harmful in small amounts. Indeed, small doses are easily assimilated by invalids. The prophet Mohammed was probably correct when thirteen hundred years ago he said, "In wine are both advantages and disadvantages to men, but the latter outweigh the former."

During alcoholic fermentation a number of by-products result and these are separated when weak alcohol is distilled. Chief of these is *fusel oil,* which was formerly considered a waste product in the alcohol industry. It contains mainly two higher alcohols, butyl alcohol and amyl alcohol. Both are used as solvents, e.g. for nitrocellulose lacquers, and with the other alcohols present in fusel oil for the preparation of artificial fruit essences. These are sweet smelling esters, or compounds of acids with alcohols. Amyl acetate is the principal ingredient of pear essence, ethyl butyrate of pineapple essence; and amyl iso-valerate of apple essence.

The butyl alcohol-acetone fermentation is one of the most interesting of the industrial fermentations, and of recent years it has become one of the most important and most widely studied. During the war acetone was required in large amounts for making cordite. A micro-organism capable of converting starch into acetone had been discovered at the beginning of the century by Fernbach, and with similar organisms it was pressed into service in nearly all the belligerent countries to supplement the supplies of acetone. It is curious that although this is an important peace-time chemical its production by a cheap fermentation method was delayed until 1914. In the process devised by Weizmann a mash prepared from grain is sterilised, and inoculated with a culture of *Bacillus granulobacter,* which ferments the starch in the grain with the production of acetone and twice its weight of butyl alcohol (butanol); hydrogen and carbon dioxide are also formed. Starting as a war industry for the production of acetone, with butyl alcohol as a by-product, this fermentation process has continued and is now employed primarily to supply butyl alcohol as an industrial solvent and as the source of butyl acetate and butyl propionate, both of which are used in the manufacture of perfumes and flavourings. The cultures of the bacillus were obtained from cow manure, slaughter house refuse, and from milk intended for human consumption. The butyl alcohol-acetone bacillus is said to be *anaerobic,* that is, it ferments organic matter in the absence of air. Enzymes present in the bacillus break down the organic matter and the energy liberated is used by the organism for growth and propagation. Certain species of moulds have also been employed for fermenting starch into acetone without the production of butyl alcohol. Synthetic butyl alcohol obtained from acetylene has been put on the market recently by German firms; it is marketed as butanol.

Another by-product of normal alcoholic fermentation is glycerin, three parts of which are formed from every hundred parts of sugar fermented. Although Pasteur noted this in 1860 no attempts were made to increase the yield of this valuable substance until the war years. Necessity is the mother of invention. Germany, faced with a shortage of fats which have always been the most important source of glycerin, turned to the yeast cell for help. Increased interest was taken in yeast fermentations, and eventually factories were established producing glycerin as the main product rather than as a by-product of fermentation. Neuberg showed in a series of classic fermentation studies that in the presence of sodium sulphite yeast converts sugar mainly into glycerin, with alcohol as a by-product. Over 2,000,000 lbs. of glycerin were produced monthly in Germany by this method.

It is well known that weak alcoholic liquids sour on exposure to the air to form vinegar. The change, which is brought about by certain bacteria (*Mycoderma aceti* and *Bacterium aceti*), is due to the oxidation of the alcohol to acetic acid. Wine gradually changes to vinegar merely on exposure to air because the spores of the bacteria are always present in the atmosphere and settle in the wine. Pure alcohol, or alcohol dissolved in water, is unfermentable; nitrogen, phosphorus and sulphur compounds are necessary for the growth of bacteria and these elements are absent from alcohol, although they are present in wine. Wine vinegar is made in France by adding wine to strong vinegar contained in casks with openings to admit air, which is essential for the process. The vinegar contains the necessary bacteria to convert the alcohol of the wine into acetic acid. In this country vinegar is usually made from malt, which is mashed and first fermented by yeast to produce weak alcohol. Nitrogenous matter and salts suitable for the growth of the acetifying bacteria are added to this, and the resulting liquid allowed to trickle into a large, well aerated vat containing beech wood shavings, or basket work, inoculated with the bacteria. The liquid running out of the bottom of the vat is returned to the top and repeatedly circulated through it until most of the alcohol is converted into acetic acid. Vinegar is also made from cider. A certain species of mould, called *Aspergillus niger* by the biologist, is able to convert sugar solutions into an acid known as *gluconic acid.* This has been proposed as a substitute for vinegar; it has a higher nutritive value.

Acetic acid for industrial and scientific uses is never made from vinegar, which at the most contains 10 per cent of the acid, but by the distillation of wood (p. 155), or by a synthetic process from acetylene gas. When this is passed into water containing sulphuric acid and a little mercuric sulphate, a compound called acetaldehyde is produced, and this can be oxidised by the oxygen of the air into acetic acid. A catalyst, manganese acetate, is used to facilitate the oxidation.

Micro-organisms are of inestimable value in the food industry, provided their activities are controlled. It is when they run riot that the jam goes mouldy, milk turns sour, butter becomes rancid and meat putrefies. Milk, the perfect food for man, is also a perfect food for bacteria because it contains mineral salts, carbohydrates, fats and proteins. Bacteria thrive on milk; indeed this is one of our most infected foods. Milk is germ-free in the udder of the cow and in the absence of bacteria it can be kept free indefinitely. Pasteur kept sterile milk in contact with air for years. The keeping qualities of milk depend upon the number of bacteria present, and ever since the dairyman has become acquainted with this fact he has attempted to keep the milk as pure as possible. In hygienic dairies scrupulous cleanliness is observed; the vessels and utensils are sterilised, udders washed before milking and personal cleanliness of assistants insisted upon. Certified milk is guaranteed to contain less than 30,000 organisms per cubic centimetre —17,000,000 per pint! One hesitates to think of the number of micro-organisms in milk from a dirty farm after it is about 48 hours old. Milk is pasteurized by heating it to 63° C. (145° F.) and then rapidly cooling it. (Plate 37.) This does not destroy all the bacteria—it would be necessary to keep the milk at boiling point for many hours for this—but renders disease bacteria harmless.

Milk that has been soured by special yeasts is highly esteemed in certain parts of Asia and Europe. *Koumiss* is made in the Caucasus region by fermenting mare's milk with *kephir* granules, which contain yeast and bacteria living together for mutual benefit—biologists call this social attraction *symbiosis*. The yeast produces alcohol and the bacteria make lactic acid (the acid present in sour milk); at the same time enzymes secreted by the organisms digest the proteins of the milk to form an easily assimilated and highly nutritious beverage. It is more nutritious than beer.

The production of lactic acid in the souring of milk is one of the commonest of fermentations produced by micro-organisms. Certain bacteria, the *Lactobacilli*, possess the power of converting milk sugar into lactic acid. The curdling of milk, which occurs prior to its digestion in the stomach, is brought about by the enzyme called *rennin*. This is present in the rennet of the housewife. Rennin acts upon casein, the protein of milk, to form paracasein, which forms the clot, and whey. It is interesting to note that the calcium salts of milk, which are essential for the formation of bone in young children and animals, are carried down with the paracasein. This curdling of milk is important in the manufacture of casein, and as the preliminary process in the production of cheese. After the milk has curdled the curd is separated from the whey, either by mechanical division (soft cheese), or by stirring and heating (cooked cheese), and then allowed to stand. Sometimes the whey is pressed out, in which case the product will be a Dutch cheese. The curd is salted, pressed in a cheese mould and allowed to "ripen," the difference in the various cheeses being due to the changes going on during the ripening process. The moist curd forms a favourable breeding ground for the innumerable micro-organisms and their spores floating about in the air. They settle down comfortably and proceed to pour out enzymes capable of breaking down the casein into simpler proteins, alcohols and esters with a characteristic cheesy flavour. Many microbes excel in producing traces of these savoury substances. The whole process is exceedingly complicated and as yet imperfectly understood. The lactic acid-forming bacteria are important in the production of the cream and soft cheeses, and in the ripening process of the curd. Special cultures of these bacteria are isolated and introduced before the ripening stage, e.g. *bacillus of Massol*. Micro-organisms also settle and develop on the surface of the cheese and gradually work their way inwards. The green cheeses, such as Gorgonzola and Roquefort, owe their colour to the green spores of the mould *Penicillium.* Camembert and Limburger cheese contain small quantities of indol, a foul smelling body, formed during the decomposition of casein.

Casein can be made from milk by curdling it with acids, and this method is usually adopted in its industrial preparation. It is used in making patent foods—*Sanatogen* and *Plasmon* are mainly composed of it—and casein plastics. The latter are made by treating casein with formaldehyde and subjecting to high pressures when it becomes horn-like in appearance. The product can be coloured with pigments, and as *erinoid* and *galalith* it is used as a substitute for horn, bone, ivory, ebonite, amber and tortoiseshell. Combs, beads, knife handles, buttons, umbrella handles, cigarette holders and many similar articles are made from it. Unlike celluloid it is non-inflammable, but is not elastic, and cannot be made into thin films. Mixed with sodium bicarbonate, casein is also used for making size and distempers. The latter consist of casein mixed with slaked lime and suitable pigments.

The ripening that cream undergoes in the making of butter depends upon the work of micro-organisms. Hitherto the cream was exposed to the air and any air-borne bacteria allowed to settle on it. This gave uncertain results, since sometimes undesirable bacteria developed and gave the butter a smoky or fishy taste. In all up-to-date dairies special cultures of micro-organisms are added to produce the right degree of acidity and flavour and at the same time the temperature is controlled; this is an important factor in all fermentation processes, because it not only determines the rate at which the particular fermentation takes place but also the products. The rancidity of butter is due to the development of undesirable bacteria which split up the butter fat into glycerin and butyric acid, a thick liquid with a rancid smell of perspiration. This acid is also formed in the bacterial decomposition of the proteins in cheese, and by the action of the butyric bacillus, *Bacillus butylicus,* on lactic acid or on sugar. The rancidity of all fats is due to bacterial action.

One of the greatest problems of the civil engineer is the effective disposal of sewage in large towns. It is only by studying the habits of the bacteria that feed upon it that the problem has been solved. In the case of small communities the sewage can be rapidly disposed of by pumping it on to the land where the soil bacteria feed upon it, converting it into materials that afford a rich nutriment for growing crops. The liquid sewage effluent that drains through the soil has all its objectionable qualities removed and does not contaminate drinking water. Bacteria thus enable man to return to the soil what he takes from it in the form of food crops. In the case of big towns, however, special means are adopted to dispose of the sewage, which may contain as much as 12,000,000 bacteria per cubic centimetre. Before 1916 the sewage was allowed to trickle from the sewage tanks through filter beds of coke or sand, which, by exposing a large surface to the air, enabled the bacteria to develop rapidly and ferment the nitrogenous bodies and carbohydrates of the sewage into harmless substances, e.g. methane, ammonium compounds and nitrates. Most large cities now employ the activated sludge process, which was invented in 1913, and introduced three years later. In this process the sewage is well aerated to hasten the decomposition set up by the bacteria; they feed and develop more rapidly with an increased supply of air and thus ferment the sewage at a quicker rate. The sludge that separates during the fermentation can be dried and used as a fertiliser, or inoculated with special bacteria, which decompose it with the production of combustible gas. Much power gas is now made on a large scale from sewage sludge for driving internal combustion engines. It consists mainly of methane, and is used in Birmingham and some American cities for heating purposes. Thus do bacteria convert the obnoxious into the useful. Power gas is also obtained by the fermentation of vegetable waste, the dry matter of which is largely cellulose. The residue is dried, inoculated with suitable bacteria and sold as a soil fertiliser. London sewage sludge is dumped into the sea and the nitrogen that it contains thereby lost. In Birmingham the nitrogen is recovered.

We have noted the relationship between bacteria and soil fertility (p. 181). Some—the putrefactive bacteria—are concerned with decomposing animal and plant proteins present in the soil into ammonia, which is then oxidised by other bacteria into nitrites and nitrates. These bacteria, which play such an important part in agriculture, are the active agents of sewage purification. The nitrogen-fixing bacteria, the *Azotobacters*, which develop in the nodules on the roots of leguminous plants, assimilate atmospheric nitrogen and enrich the surrounding soil with combined nitrogen compounds. Many patents have been taken out for the "biological fertilisation" of the soil by applying special cultures of these bacteria to impoverished ground. Fertilisers are prepared by mixing together peat, phosphates, protein and carbohydrate materials and inoculating the mixture with cultures of the nitrogen-fixing bacteria. Some years ago patents were taken out for synthesising nitrates from ammonia by means of the nitrifying bacteria, but such a bio-chemical method could never compete with the present catalytic oxidation of ammonia to nitric acid and nitrates (p. 201). In this case the chemist has improved upon the methods of bacteria. It is only rarely that he can do this.

Among our other soil friends are the iron and sulphur bacteria. The former derive their energy from the oxidation of iron compounds in the soil, and they convert them into a form that plants can assimilate. Plants need iron for the formation of chlorophyll. The iron bacteria, which are literally full of iron oxide, occasionally become serious pests in water reservoirs and pipes, in which they deposit accumulations of rust, or hydrated iron oxide. The *Beggiatoa,* or sulphur bacteria, may contain as much as 90 per cent of sulphur stored up within their cells. It is formed by the oxidation of that foul-smelling gas, sulphuretted hydrogen, which is given off during the putrefaction of proteins. Most proteins contain sulphur, but this can only be taken up by plants in the form of sulphates. Plants absorb sulphates, nitrates, phosphates, carbonates and water from the soil, and carbon dioxide from the air, and by a series of very complicated changes build up proteins, carbohydrates and fats. When the plant proteins return to mother earth, either directly or through animals, putrefactive bacteria seize upon them and convert them into ammonia, sulphuretted hydrogen, comparatively simple nitrogenous bodies called amino-acids, and the putrid-smelling indol and skatol. The fetid odour accompanying putrefaction is due to the presence of the two latter. The sulphur bacteria then complete the sulphur cycle by oxidising the sulphuretted hydrogen to sulphur and sulphates. Putrefaction and decay are truly wonderful processes. They are the means by which Death passes into Life. The living organism that has served its purpose dies and is resolved into the elements from which new forms of life are built up.

Bacteria and moulds are the close allies of the tanner and the linen manufacturer. In the preparation of leather, skins and hides are first soaked in lime-water to remove hair, and if old, rank lime-water is available so much the better since it is teeming with useful bacteria. They break down the surface cells of the skins and facilitate the removal of hair. The skins are then washed and *bated* or *pured*. This was formerly done by soaking in a bath of dog or bird dung, the bacteria of which fed upon and dissolved out the softer portion of the skin, leaving the fibrous material or coriin. This forms leather when tanned. Dung is now being replaced by special preparations from micro-organisms and by pancreas extract (pancreatin). A special protein-digesting enzyme is often extracted from the mould *Aspergillus wenti* for the purpose of bating hides. Hides are tanned either with infusions of the bark of certain trees, e.g. oak, hemlock, sumach, or with chromium salts, which give the leather a green colour. Thin leathers, such as glacé and kid, are tanned with alum.

Linen is made from flax by *retting*. The flax is soaked in water and the bacteria that develop secrete an enzyme, *pectinase*, which breaks down the pectin (p .233) binding the flax fibres together. This process is now controlled by introducing special bacteria into the retting tanks. Pectin is employed to make jellies and jams set. It is largely produced from the waste of cider and vinegar factories, from beet sugar waste, or directly from carrots by extraction with organic acids, such as citric or tartaric. The product contains starch and protein as impurities, and these are removed by special moulds that decompose these substances but not the pectin.

Straw can be fermented by certain micro-organisms in presence of chalk to produce the combustible gas, methane, and this process has been utilised on a small scale for lighting purposes. Other organisms convert straw into humus, which can be applied to the soil as a fertiliser. There are many other ways in which micro-organisms find useful employment. Moulds are used as a source of diastase for separating the fibroin (p. 238) of real silk; to remove excess size from fabrics; and in the canning industries to clarify jellies. Ehrlich, a German chemist, has proposed using micro-organisms to effect the synthesis of one of the constituents of attar of roses. A curious patent has recently been granted in America for making leather substitute by tanning compressed bacteria mixed with cork. Citric acid, which up to the present has always been made from lemon-juice, can be prepared by the action of certain fungi (*Citromycetes*) on sugar and carbohydrates. The acid is used in calico-printing, for medicinal purposes, and for the manufacture of effervescent and cooling drinks.

Far from being a source of profit, micro-organisms can be a source of loss and annoyance to the household and to industry. They cause meat and fish to putrefy and jams to liquefy and go mouldy. Obnoxious bacteria may also develop in the products of the dairy, brewing and food industries. Meats and fish are smoked or salted to prevent, or at any rate retard, the growth of the organisms of putrefaction. In the preparation of canned foods care is taken to sterilise the food before sealing the tins. This is effected by steam heating. As soon as the tins are opened germs from the air settle on the contents and in a short time turn it bad. Food cannot be sterilised by keeping it in a refrigerator. A low temperature restricts the development of micro-organisms and consequently the food keeps longer, but the micro-organisms are not destroyed. Eggs are decomposed by the action of bacteria, and their keeping qualities largely depend upon sanitary conditions and upon temperature. The shell, being porous, enables bacteria to penetrate to the interior and there set up a decomposition of the proteins. Eggs can be preserved for considerable periods by stopping up the pores with water glass, or by keeping them in cold storage. It has been found, however, that bacteria can grow on egg shells at normal cold storage temperature. Preserved eggs are never as good as fresh eggs, because the protein gradually breaks down on keeping to form definitely harmful products.

Since wood consists mainly of cellulose it forms a favourable medium for the development of cellulose-digesting organisms. These cause considerable damage to wood, especially during storage. Timber can be protected against the ravages of these microscopic invaders by impregnating it under pressure with antiseptic liquids. Tar oils, creosote, mercuric chloride (corrosive sublimate) sodium fluoride, and copper sulphate are employed for this purpose. Allied to the rotting of wood is the mildewing of textiles. The detrimental action of micro-organisms can be seen in tent, sail and aeroplane fabrics.

The sugar refiner has special reasons for disliking bacteria. They often settle on the pressed juice from the canes and beets, and prevent the crystallisation of the sugar. This is because they secrete the enzyme *invertase*, which hydrolyses cane sugar into *invert* sugar, a mixture of glucose (grape sugar) and fructose (fruit sugar), which only crystallise with difficulty. This change is known as the inversion of cane sugar. Invertase preparations from moulds are useful, however, in making concentrated sugar syrups. In this case, it is not desirable that the sugar should crystallise out. Invertase is said to be used commercially in Canada and the United States.

Another objectionable group of micro-organisms—the thermophilic or heat-loving bacteria—cause the spontaneous ignition of hayricks and cotton waste. The organisms bring about the oxidation of the hay and cotton, and if the heat generated during the process is not dissipated the temperature rises, oxidation becomes more rapid, and finally the mass bursts into flame.

The application of micro-biology to chemical industry has only just begun. Micro-organisms even act upon coal and hydrocarbons; some can utilise 80 per cent of soft paraffin and others can oxidise such stable compounds as benzene and naphthalene. There is evidently, then, no limit to the chemical processes that they can bring about. Sir William Pope, the eminent Cambridge chemist, has pointed out that substances prepared by the aid of the enzymes of plants and micro-organisms cost much less than those prepared by the chemist synthetically in the laboratory and factory. This is because the organisms use low-grade solar energy, which costs nothing, and demand neither wages nor an eight-hour day. It is possible that by intensively exploiting the chemical reactions brought about by micro-organisms, we shall enjoy some relief from the high cost of energy now obtained from fuel, and from the increasing demands of the worker for shorter hours and higher wages. The latter, even if justified from the economic standpoint, do not lower production costs.

CHAPTER XIII

CHEMISTRY VERSUS DISEASE

THE chemist has long been confused with one who is more appropriately called a *pharmacist,* that is a dealer in drugs. In Germany the compounder of medicines is known as an *apotheker,* and in France as a *pharmacien.* But in this country the title of Chemist and Druggist, assumed by the pharmacist, or apothecary as he was once called, is invariably associated in the public mind with a seller of medicines. This is not surprising since chemistry has been associated for centuries with medicine. Even in the last century some of the foremost chemists received their first impressions of chemistry in an apothecary's shop. Scheele, Davy, Berzelius, Wöhler and Liebig approached chemistry through pharmacy, and until the middle of the last century professors of chemistry usually possessed medical qualifications. In the eyes of the law a "chemist" is still one qualified to sell drugs.

The art of healing was associated at a very early date with a crude empirical form of chemistry. It has been said that chemistry had its origin in temples where priests performed chemical experiments with a view to making medicines. Chemical processes have been employed from time immemorial for extracting juices from plants and for preparing mineral medicines. The ancients possessed a knowledge of both vegetable and mineral drugs and their uses, although Hippocrates (*c.* 400 B.C.), the Father of Medicine, was none too eager to administer them. He believed in the *healing power of nature*—a phrase that actually occurs in his writings—and preferred diet, exercise and natural methods to drugs. Most of the drugs employed were of vegetable origin. Mineral remedies were in use, however, and included compounds of zinc, lead, copper and possibly mercury. An extensive medical herb lore has come down to us from the Greeks, mainly through Dioscorides (1st to 2nd cent. A.D.) who mentions about five hundred plants with medicinal virtues. It is remarkable that thirty-seven per cent of our Pharmacopœia was known to the later Greek medical men. Medicine declined in Europe during the Middle Ages, partly owing to the anti-scientific attitude of the Church and partly because the practice of medicine was largely in the hands of monks, who allowed the theoretical knowledge garnered by the ancients to lapse. The curse of science—and medical science is not exempt—has always been the so-called "practical man" who only acquires what he considers to be practical knowledge without understanding the fundamental principles on which it is based. Mediæval medicine sought the immediate relief of the patient and threw overboard anatomy, physiology and chemistry. The healing art became reduced to an absurd rule of thumb practice. But the flame kindled by the Greeks was kept alight by Islam, whose followers did much to preserve and extend medicine. They introduced many new drugs, so that by the close of the fourteenth century about fifty per cent of the naturally occurring drugs known to-day were in use.

The period in the history of chemistry known as *iatro-chemistry* (from the Greek *iatros*, a physician) was inaugurated by that turbulent figure of the early sixteenth century, Paracelsus (1493-1541)—self-styled Philippus Aureolus Theophrastus Paracelsus Bombastes von Hohenheim. He emphasised the importance of studying chemistry as a means of preparing drugs and medicinal remedies. He diverted the attention of chemists from trying to make gold to preparing medicines. Chemistry, said Paracelsus, was henceforth to be the handmaid of medicine. It was apparently not worthy of study for its own sake; it was a means to an end, a mere Cinderella science. But subservience to medicine was better than subservience to the foolish obsession of gold making, and chemistry passed from the hands of charlatans into those whose true calling was medicine. The change was for the good, because the iatro-chemists collected an enormous number of chemical facts, and since the substances they prepared were for medicinal purposes they had to be carefully purified. These workers thus eventually grasped the idea of chemical purity and chemical individuality, two valuable concepts that played an important part in the subsequent development of chemistry.

Paracelsus himself introduced several new remedies. It is said that he used mercury as a specific against syphilis, which was ravaging Europe in the sixteenth century. He also used medicines containing iron, arsenic, sulphur, and laudanum, or tincture of opium. From this time onwards indiscriminate dosing with drugs became a vice, and even in some quarters to-day drugs are given to remove symptoms rather than cure disease. An American doctor has summed up the situation in the following words:

> I firmly believe that if the whole *materia medica* could be sent to the bottom of the sea, it would be all the better for mankind and all the worse for the fishes.

The iatro-chemists introduced chemical interpretations to account for the changes in the body in both health and disease. For many centuries the humoral pathology of Hippocrates had guided medicine. It was assumed that disease resulted from disturbances in the proportions and properties of the four humours or liquids of the body: *blood, yellow bile* (choler), *phlegm,* and *black bile* (melancholy). According to the prevailing humour, the followers of this doctrine distinguished sanguine, choleric, phlegmatic and melancholy temperaments. The iatro-chemists drew attention to the fact that many of the processes going on in the body were akin to fermentation—a view that time has confirmed. Our life, from the womb to the dust, in every breath we draw and in every moment of our conscious and unconscious existence, is indissolubly connected with the most complex chemical changes.

The discovery of America resulted in the introduction of many new vegetable products into medicine, among them cinchona (from which we obtain quinine), ipecacuanha, and tobacco, which was long used as a narcotic.

Gradually chemistry became freed from the trammels of medicine and eventually attained the position of a science worthy of study for its own sake. Since that time it has rapidly progressed, so that to-day the physician is entirely dependent on synthetic or creative chemistry for his most efficacious drugs, his anæsthetics, his antiseptics, and even for his instruments. It was a chemist—Pasteur—who gave the scientific demonstration of the germ doctrine of disease, introduced serum-therapy, and laid the foundations of our knowledge of immunity.

The physician of to-day, unlike his predecessors, is able to administer drugs in a " pure form." This means that not only can drugs be obtained unadulterated, but that the chemical substances to which they owe their properties can be isolated and standardised, and hence a given dose can be administered. Most drugs used in medicine are of vegetable nature, and since their composition varies from time to time the administration of a definite dose is difficult. The term *drug* is a bad one. It reminds one of the days when drugging symbolised medicine and when the use of drugs was empirical and even nonsensical. Charlatans under the cloak of herbalists still flourish by selling " vegetable drugs " which they assert are safer and more beneficial than drugs of mineral origin. The use of the latter, they state, is " contrary to nature ". This is sheer nonsense. Other quacks advertise "vegetable compounds" that contain no drugs.

By a drug we usually mean a substance that increases or decreases the function of one or more organs or tissues. The possibility of giving drugs in a pure form resulted from the discovery, early in the last century, that plants owe their poisonous and medicinal properties to the presence of certain *active principles,* which can be extracted by chemical means. The isolation of these was important as it opened up the possibility of accurate dosage, and enabled the physiological effects of drugs to be quantitatively measured. This was impossible when only the crude vegetable drug of unknown strength and composition was available. Thus arose the science of *pharmacology,* which deals with the nature and physiological action of drugs. Since the middle of the last century the study of this has been mainly in the hands of German investigators.

After the chemist analysed the active principles occurring in plants and determined their structure or constitution, attempts were made to produce them synthetically. But for many years chemical synthesis had not developed sufficiently to enable many of the complex principles to be built up. Indeed, many well-known drugs of vegetable origin which are still used in large quantities to-day have not yet been synthesised, e.g. quinine, morphine, and the active principles of digitalis. After the rapid development of organic chemistry a large number of the active constituents of not only plants but animals was synthesised, mainly from coal-tar products. Certain of the active principles can only be extracted from the natural sources by very complex chemical processes and sometimes there are special obstacles in the way of their complete purification. These difficulties are surmounted by the synthetic preparation of the drugs in the laboratory. In addition, numerous other synthetic products have been introduced into medicine that are unknown in nature, and in many cases they have replaced the older drugs. Aspirin, novocaine, veronal, β-eucaine and heroin are essentially laboratory products; they are not found in nature. Many of these new synthetic drugs are made from by-products obtained in the synthetic dye industry.

Surgical science has been dramatically revolutionised by the discovery and application of anæsthetics. Modern surgery rests upon anæsthesia and asepsis. Apart from sparing the patient much suffering anæsthetics enable the surgeon to take more time over delicate operations. Before their adoption speed was of primary importance and hence errors of judgment were frequently made. Although ether was known in the fourteenth century, when it was prepared by the action of sulphuric acid on alcohol, it was not employed as an anæsthetic until 1842, when Dr. Long of Georgia used it in private practice. In 1847 Sir James Young Simpson of Edinburgh was using it for obstetric purposes. Shortly afterwards he employed chloroform, which Liebig had discovered in 1831 by acting on alcohol with chloride of lime (bleaching powder). Incredible as it may seem, there were many who objected to these pain-relieving agents on the grounds that man was intended by God to bear pain. Simpson, who was somewhat witty, reminded these people that Adam was put to sleep before his rib was removed.

In 1800 Sir Humphry Davy discovered that nitrous oxide, or laughing gas as it is sometimes called, has anæsthetic properties. After trying its effect on himself he wrote the following lines on recovering consciousness:

Not in the ideal dreams of wild desire
Have I beheld a rapture-wakening form;
My bosom burns with no unhallowed fire,
Yet are my eyes with sparkling lustre fill'd;
Yet is my mouth replete with murmuring sound;
Yet are my limbs with inward transport filled
And clad with newborn mightiness around.

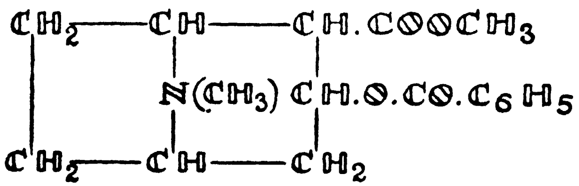
Nitrous oxide, which is usually used mixed with oxygen, does not produce such deep anæsthesia as ether or chloroform and is hence used in dentistry.

In 1923 it was found that the gases acetylene (sold as *narcylen*) and ethylene can be used, if mixed with oxygen for inducing anæsthesia. The application of these is still in the experimental stage.

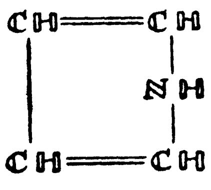
For many purposes, in general surgery and in dentistry, it is more convenient to administer a local anæsthetic, which produces insensibility to pain only in the area of operation. Two methods are employed to inject the anæsthetic. A solution of it is either introduced by a hypodermic syringe directly into the region where anæsthesia is required, and the nerve terminals paralysed; or an injection is made near a nerve trunk, which renders the region supplied by that nerve insensible to pain. Local anæsthesia dates from 1884, when cocaine was used in eye surgery. When Pizarro conquered Peru his men observed that the Indians chewed the leaves of a certain plant to enable them to withstand fatigue and hunger. The plant was later cultivated in Europe and named *Erythroxylon coca;* it is the cocaine plant. Although the physiological effects of cocaine were well known, it was not until 1860 that Neumann succeeded in extracting the drug in a crystalline form from coca leaves. At first the drug was used as a stimulant—continued use of it leads, as is well known, to mental and physical degeneration—and in 1884 Koller, of Vienna, discovered that it is a powerful and rapid local anæsthetic.

The enthusiasm aroused over the new drug among the medical profession was short-lived. Surgeons soon observed that cocaine is toxic and may even cause death occasionally, that it is habit-forming, and that its solutions readily go mouldy. It cannot be sterilised by boiling, because this destroys it. Cocaine was nature's only local anæsthetic and it had failed.

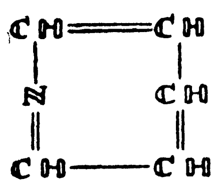
Here was a chance for the chemist to improve on nature. To produce a drug with the effects of cocaine, yet without any of its objectionable properties, necessitated a knowledge of its structure and synthesis. By dint of industry and perseverance on the part of some German chemists including Merling, Einhorn, Ladenburg and Willstätter, the structure of cocaine has been determined and its synthesis achieved. It has the structure



For some time chemists have been aware that the physiological properties of drugs are, to a large extent, dependent upon the presence of certain groups of atoms in the molecule.[1] The first step was to find out what parts of the cocaine molecule are necessary to induce anæsthesia. It was discovered that there are three fundamental groupings in the cocaine molecule. Firstly, the group or ring of atoms on the left derived from *pyrrole*—



and present in nicotine. Secondly the group or ring of atoms on the right, which is common to a number of active principles of vegetable drugs, and which is derived from *pyridine*—



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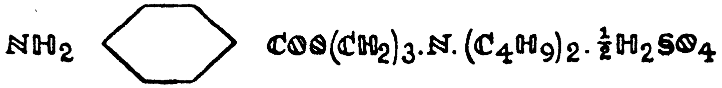
[1] Compare structure of dyes and colour, p. 280.

The pyridine grouping is present in *coniine*, the active principle of the poison hemlock, by means of which Socrates was put to death. This grouping is responsible in part for the anæsthesia produced by cocaine. The third group is the $O.CO.C_6H_5$, or *benzoyl group*, situated on the right hand side of the cocaine molecule and particularly associated with its anæsthetic properties.

Bearing these facts in mind it has been found possible to synthesise drugs similar in action and chemical constitution to cocaine, but without the harmful properties of that substance. The discovery of these new drugs is one of the triumphs of the application of synthetic chemistry to the science of pharmacology. Among the new drugs are *β-eucaine, holocaine, stovaine, alypine, orthoform, anæsthesin* and *novocaine*. They are all benzoyl derivatives. β-eucaine, which is made from acetone and ammonia, resembles the right hand part of the cocaine molecule. Holocaine, or as it is sometimes called phenacaine, is a somewhat toxic anæsthetic made from the drug *phenacetin;* it has a limited application in eye work. Stovaine, a well-known anæsthetic employed for spinal anæsthesia, is also made from acetone.

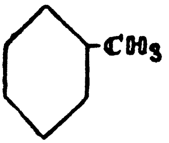
Novocaine, now the most valued of all local anæsthetics, was first synthesised in 1905 in Germany by Einhorn. It possesses most of the properties of cocaine, but is less toxic, cheaper, more stable and is not habit forming. When injected with adrenalin (p. 355) the anæsthesia produced is not inferior to that brought about by cocaine. Consequently it has been adopted in the medical and dental world in preference to the latter. Unfortunately novocaine, unlike cocaine, does not produce *surface anæsthesia* when it is placed on the tissues. Thus it could not be employed for eye and nose operations, and for this purpose it did not rival cocaine. Several new synthetic drugs were introduced after the discovery of novocaine, but most of them were found to be inferior to this drug and to cocaine.

The next local anæsthetic of note was discovered as a result of the increased demand for acetone during the war. We have seen that large quantities of this substance were prepared by a fermentation method, and that butyl alcohol resulted as a by-product. Another alcohol, *trimethylene glycol*, was then being produced as a by-product in the soap works. These two alcohols, and other intermediates, formed the starting point for the preparation of new cocaine substitutes. The efforts of chemists were crowned with success in 1920 when *butyn*

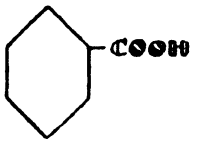


was discovered. The three methylene groups—$(CH_2)_3$ or $CH_2.CH_2.CH_2$—are derived from trimethylene glycol, HO. $CH_2CH_2CH_2OH$; the two butyl groups, C_4H_9, come from butyl alcohol, C_4H_9OH. This new drug, similar in structure to novocaine although more complex, was found to be more effective than cocaine and free from some of its disadvantages. On the other hand, its effects are superior to those of novocaine, both in the degree and rapidity of the anæsthesia produced. This renders it particularly suitable for dental work.

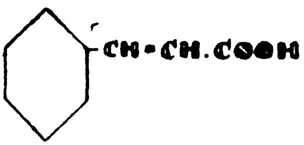
Apothesine resulted from researches carried on during the war to find cheap and effective substitutes for cocaine. In the early war years novocaine was difficult to obtain since its manufacture had hitherto been a German monopoly. Most of the local anæsthetics then in use were derivatives of benzoic acid, a coal-tar product obtained from toluene. It occurred to two American chemists to use cinnamic acid, which is a derivative of benzoic acid, as a starting point.



Toluene

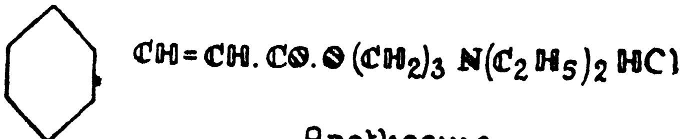


Benzoic acid



Cinnamic acid

Apothesine resulted from a combination of this acid, trimethylene glycol, ordinary alcohol, ammonia and hydrochloric acid.

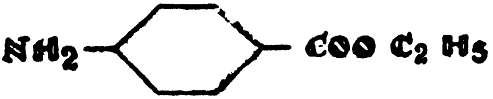


Apothesine

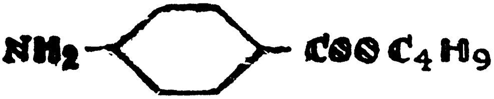
It is more effective than novocaine, but more toxic. *Tutocaine* and *psicaine* are two other anæsthetics of this class that have been recently introduced. The former, which is somewhat similar in composition to novocaine, can be applied in smaller doses than this drug. Psicaine is very closely related to cocaine itself and has most of its properties, although it is said not to be habit-forming. Cocaine is a complicated sort of substance and by arranging the atoms composing it in different ways in space, eight forms of it are obtainable. One form is natural cocaine; another form is psicaine, a synthetic product first obtained by Willstätter, who has done much work in this field of chemistry.

When a local anæsthetic is injected into a particular region of the body, it tends to diffuse into the blood stream with the result that the duration of anæsthesia is shortened and the toxic effects are increased. The drug adrenalin constricts the blood vessels and, if administered in conjunction with a local anæsthetic, it diminishes the diffusion of the latter into the blood, decreases the toxic effects, increases the period of anæsthesia, and checks bleeding resulting from the operation. Adrenalin is now used with most of the local anæsthetics. The abandonment of the eucaines and certain other anæsthetics has been mainly due to their incompatibility with adrenalin.

There is another group of local anæsthetics that is employed in general medicine in the form of dusting powders, lozenges and ointments for the relief of pain. These are the insoluble local anæsthetics used in alleviating complaints of the nose, mouth and internal organs. They are comparatively simple bodies, mainly derived from benzoic acid. *Anæsthesin*, or *benzocaine*,



made from benzoic acid, nitric acid and alcohol, is the basis of many pain-allaying ointments. It was discovered in 1890 by Ritsert, but some ten years elapsed before its value was recognised. A whole series of local anæsthetics possessing antiseptic properties was discovered towards the end of the nineteenth century by Einhorn in Germany. Orthoform, nirvanin, and holocaine are used in the treatment of burns and denuded skin areas; they are esters of benzoic acid derivatives. We can go up the series from the ethyl ester, through the propyl, butyl, amyl and higher esters. The most effective group is the butyl, C_4H_9, which is present in *butesin*,



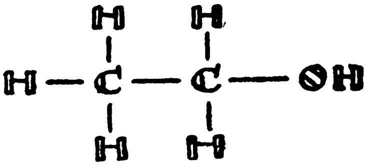
one of the post-war drugs.

Synthetic organic chemistry has not only produced cocaine substitutes that have all the advantages and none of the disadvantages of this drug, but it has given to medicine local anæsthetics for specific purposes. Novocaine, for example, is employed for deeper surgical work, butyn for use on mucous membranes, and the antiseptic anæsthetics for the treatment of burns and ulcers.

Until quite recently the only hypnotic or sleep-producing drugs were various preparations of opium, the dried juice of an Eastern poppy. These possessed the great drawback of being dangerous in the doses necessary to produce deep sleep, and of causing unpleasant after effects. But synthetic hypnotics have now come to the aid of the physician. The drug *chloral* was prepared as early as 1832 from chlorine and alcohol. For nearly forty years its hypnotic properties were not appreciated, and when they were, physicians found that patients ran the risk of acquiring a craving for the drug. Rossetti, it will be remembered, died from an overdose of chloral, a drug to which he was an addict. The objectionable properties of these older hypnotics induced the organic chemist to synthesise compounds with a maximum hypnotic action and a minimum of dangerous secondary effects. The history of this phase of organic synthesis is an inspiring tale of chemical achievement. Many synthetic hypnotics are known to the physician to-day, and when wisely used are neither very toxic nor unduly habit-forming.

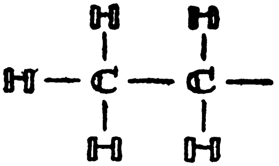
The synthesis of hypnotics and narcotics, or drugs which produce diminished mental activity bordering on the unconscious, has only been made possible by an intensive study of compounds with a known hypnotic or narcotic effect. Undoubtedly the sleep-producing properties of these drugs reside in their chemical nature. Many substances behave as hypnotics.

Among the simplest and mildest are the bromides of sodium and potassium, which are more correctly described as sedatives. These exert a soothing influence by diminishing pain or depressing vital activity. Alcohol is also a well known hypnotic, as those who have experienced its stupefying effects will testify. Now alcohol has the formula—



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & \text{—} & C & \text{—} & C & \text{—} & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

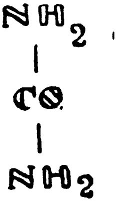
and the chemist has long been aware that the ethyl group,



$$\begin{array}{cccccc} & & H & & H & \\ & & | & & | & \\ H & \text{—} & C & \text{—} & C & \text{—} \\ & & | & & | & \\ & & H & & H & \end{array}$$

or C_2H_5, present in it has a definite action on the nerve tissue of the body. Many of our hypnotics contain one or more ethyl groups. The action of these groups on the nervous tissue is strikingly demonstrated in the case of certain dyes containing ethyl groups. They dye nerve fibres, whereas the corresponding dyes containing the ethyl groups substituted by methyl groups (CH_3—) have no effect. Alcohol is never used medicinally as a hypnotic owing to its toxic nature, the danger of habit formation, and the large amount required to produce sleep. Ethyl chloride and ethyl bromide have narcotic properties.

Urea—



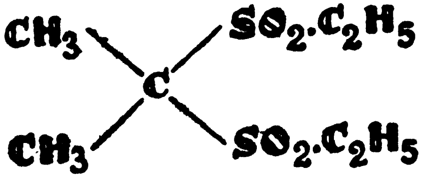
$$\begin{array}{c} NH_2 \\ | \\ CO \\ | \\ NH_2 \end{array}$$

is another substance that forms derivatives with sedative and hypnotic properties, although the compound itself is so mild that it is never used for the purpose. It is formed in the body as a waste product from the breaking down of the proteins in the food, and is extracted from the blood by the kidneys which divert it into the urine.

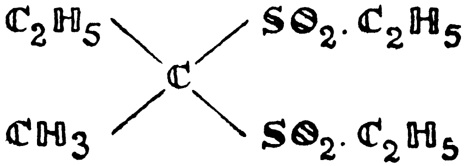
As a result of the analysis of many compounds exhibiting hypnotic properties the chemist has come to the conclusion that the bromine atom, the ethyl group, and the urea molecule are specifics for inducing sleep; and armed with this fact he has been able to build up a large number of complicated compounds that, in addition to possessing hypnotic powers, have none of the objectionable properties of the older hypnotics. At the same time it is now well established that a hypnotic must be soluble in water and in fats. A drug to be effective must penetrate the body fluids. Since hypnotics act on the nerve cells, they must be able to penetrate the nerve tissue, which is partly made up of *lipoids,* or fatty substances, and water. It has been shown that the activity of a hypnotic is proportional to the ratio of its solubility in fat to that in water.

Although chloral was the first synthetic hypnotic, it suffers from many drawbacks. Thus it has a harmful effect on the heart, is habit-forming, and has an irritating effect on the stomach. The chemist is essentially a creator—a creator of new molecules. By linking together different atoms and groups he has succeeded in making substitutes for chloral. One of the earliest was *chloretone,* made by condensing acetone and chloroform, and unlike chloral it has no irritant action. It has a sedative as well as a hypnotic action, and has been used with success in cases of sea-sickness.

The chemist has found that the presence of the ethyl group and of the urea molecule produces the best hypnotics. The drugs known as the "sulphonals" were the first important synthetic substitutes for chloral. *Sulphonal* itself,

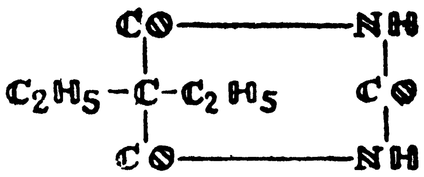


contains two ethyl groups, and as the name and formula indicate is a sulphur compound. It is made from acetone and ethyl chloride. *Trional,*



is more powerful because it has three ethyl groups. *Tetronal,* which contains four ethyl groups, should be more effective still, but since it is very insoluble this property diminishes its hypnotic effect. The sulphonals are of great importance in medicine. But they possess the drawback of passing through the body unchanged, and if used constantly tend to accumulate and produce toxic effects. The problem of toxicity is highly important from the physician's point of view. The ideal hypnotic is one that produces so little toxic effect that it can be used constantly if necessary.

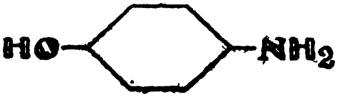
If the hydrogen atoms of urea are replaced by ethyl groups some powerful hypnotics are obtained. Diethyl-brom-acetyl-urea, or *adalin,* is used for complaints of nervous origin, but it has not attained the clinical importance of *veronal,*



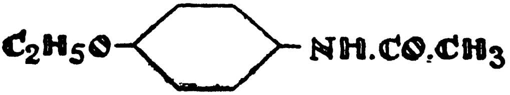
or *barbitone* as it is sometimes called. This drug, discovered in 1903 in Germany by Emil Fischer, is now perhaps more widely used than any other synthetic hypnotic. It is put on the market in the form of its compound with sodium, *veronal-sodium* or *medinal,* which, being more soluble, acts quicker than veronal itself. Another urea derivative closely related to veronal is *luminal*—or phenyl-ethyl-malonyl-urea; that is, veronal with one of its ethyl groups replaced by a phenyl (C_6H_5) group. Because of its specific action on what is known as the motor area of the brain, which controls nerve impulses, luminal is used for the treatment of certain nervous complaints (epilepsy, St. Vitus' dance).

In addition to hypnotics the physician often needs drugs to stop acute pain. These are called analgesics. Certain of these drugs were originally introduced on account of their property of reducing the body temperature in fever (antipyretic action), but it was afterwards found that in many cases they act on the nervous system and allay pain. Quinine, as is well known, reduces the body temperature in fever and is a specific against malaria. Since quinine is a naturally occurring drug—it is present in cinchona bark—chemists directed their attention to the production of compounds with properties similar to those of this drug. Curiously enough, although the formula accepted for quinine was incorrect, several compounds were synthesised on the basis of this, having an antipyretic effect like quinine, but they lacked its specific anti-malarial properties. The first successful antipyretic was synthesised by the German chemist Knorr, and appropriately called *antipyrine* instead of dimethyl-phenyl-pyrazolone, its proper chemical name. Like many of the other synthetic antipyretics it has a powerful analgesic action, and has the useful property of diminishing neuralgic pains. A valuable derivative of antipyrine is *pyramidone*, obtained by introducing two methyl groups (CH_3) and an amino-group (NH_2) into antipyrine. The cheapest of all antipyretics and analgesics are derivatives of aniline. *Acetanilide*, or *antifebrine*, is prepared from acetic acid and aniline, and its physiological effects result from the slow liberation of aniline within the body. In large quantities aniline acts upon the hæmoglobin, the red colouring matter of the blood, giving rise to toxic symptoms. For this reason, continued use of antifebrine may cause aniline poisoning.

It was discovered that when aniline, which has a strong antipyretic effect, is administered to human beings and animals, it is partially converted into a compound termed para-amino-phenol; that is phenol, or carbolic acid, with an amino group (NH_2) attached to it.



This discovery suggested that para-amino-phenol is less toxic than aniline because the body invariably overcomes the effects of toxic bodies by converting them into less noxious substances that are excreted by the kidneys in the urine. At the same time para-amino-phenol has antipyretic and antineuralgic properties. It was therefore proposed to use it, or its derivatives, for medicinal purposes. The discovery of the drug *phenacetin*,



resulted from this line of enquiry. It is obtained by replacing the hydrogen of the hydroxyl group (OH) in para-amino-phenol with the ethyl group (C_2H_5), and by replacing one of the hydrogen atoms of the amino group by the *acetyl* group $(CO.CH_3)$, which is present in acetic acid. Phenacetin was the first drug of this type put on the market and has retained the lead among antipyretics and analgesics. Numerous derivatives of this drug have been tried, among them one in which the acetyl group is replaced by *salicylic acid.* This acid, which has decided antiseptic properties was formerly used as a food preservative, and enters into the composition of many neuralgic and rheumatic specifics. *Aspirin,* or acetyl-salicylic acid, is a compound of acetic acid and salicylic acid. Its many uses are too well known to be described here. Proprietary brands of this drug are usually sold for two to three times their worth, but they are just acetyl-salicylic acid and nothing else.

In conjunction with the biologist and physician, the chemist has made invaluable contributions to the conquest of disease caused by microbial agency. When it became known that the processes of fermentation, putrefaction and decay were due to the activities of living micro-organisms, the belief that certain diseases were also caused by these minute beings gained ground. In 1877 Pasteur proved that anthrax was caused and carried by a microbe, and shortly afterwards Koch demonstrated that suppuration and tuberculosis resulted from the insatiable need of bacteria for food—which they find in the body. The new science of bacteriology sprang into being; microbes were tracked down, made prisoners and made to live in test-tubes. The organisms were made to live alone without mixing with other species. These were obtained in "pure cultures." The primary need of bacteria is food—potential chemical energy—which they obtain from the soil, manure heaps, milk, meat, or the living bodies of plants and animals. In a short time diphtheria, plague, tetanus, typhoid, and malaria were added to the list of microbial diseases. Pasteur's interest in the subject of fermentation, which was apparently first aroused by studies on the crystalline form of tartaric acid, had far-reaching results—results not anticipated even by Pasteur himself.

Since the living body is constantly exposed to disease bacteria, it is clear that some mechanism must exist by which the body resists the attacks of the microbe invaders. This mechanism is known as *immunity*. It is supposed that some people are immune to certain diseases because unknown chemical substances called *antibodies* are elaborated in their blood, and that these antibodies act on the living bacteria. When bacteria invade the body, the damage they do is not always caused by the organisms themselves but by the *toxins* or poisons that they manufacture and pour into the blood. These toxins are definite chemical substances that poison the blood; toxins have been prepared from actual disease organisms. The blood, however, produces chemical bodies known as *antitoxins* which oppose the invading germs. If the victory goes to the defenders the patient recovers; if the invaders conquer, disease results, and death may follow. Persons with a plentiful supply of antibodies for a certain disease are immune from that disease, and sometimes immunity against a specific disease can be conferred by injecting a small amount of the toxin from the bacteria concerned. This causes the blood to manufacture a specific antitoxin to resist the bacterial toxin. " Artificial " immunity against diphtheria is secured by injecting the diphtheria toxin, prepared from a culture of the diphtheria bacilli, into a horse the blood of which responds by producing antitoxins. The animal can stand in-increased doses and gradually builds up a high degree of immunity. A portion of its blood is then withdrawn and the serum (clear liquid free from blood corpuscles) obtained from it, complete with antibodies, is injected into the human body. The individual is now able to resist the onslaughts of the diphtheria germ. Immunisation against typhoid, scarlet fever and tetanus is secured in a similar manner. The immunity of individuals against diphtheria and other microbic diseases can be tested by injecting a small amount of the specific toxin into a limb of the body. If the individual is immune there is no reaction; if not immune the skin is irritated and a rash forms. This is known as the Schick test, introduced by Schick of Vienna in 1913.

The early observers noted that the virulence of disease-producing bacteria can be lowered—they become " attenuated "—if the organisms are cultivated in chemical media outside the body. Pasteur noted this in his studies on chicken cholera, and he found that the same effect could be produced by growing the organisms at higher temperatures. If injected into the body the attenuated culture of the bacteria causes a mild attack of the disease and confers immunity on the individual. Immunity can also be secured by the injection or inoculation of cultures of dead bacteria. When the blood serum of an immune individual is added to a suspension of living disease bacteria, they lose their power of movement and clump together or *agglutinate*; they are in fact killed.

Diphtheria and tetanus bacteria produce their harmful effects by pouring out soluble toxins into the blood. Most other disease bacteria only give up their toxic products when they die.

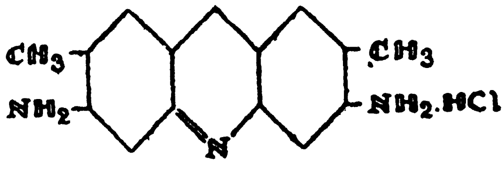
A most remarkable chemical defence against bacterial invaders is put up by the white blood corpuscles or *leucocytes* of the blood. The blood consists of a fluid, the serum, in which are suspended red and white corpuscles or cells. Millions of disease bacteria are ready to swarm into any breach in man's protective armour, the skin, and once they gain an entry, war to the death is carried on between them and certain of the leucocytes, which Metchnikoff, the great Russian scientist who succeeded Pasteur in Paris, calls the *phagocytes.* The more immune the individual the more effective are the phagocytes in resisting the invasion of the hostile bacteria. The blood has two means of defence. It prepares antibodies in the serum to neutralise the bacterial toxins, and it possesses efficient soldiers in the form of the phagocytes or *cell eaters.* They are attracted from remote parts of the body, even from the marrow of the bones, by the chemical changes occurring at the site of infection, and accumulate at the point of danger. Here they literally surround the invaders, take them into the cell body and there dissolve or digest them. This action has actually been observed by Metchnikoff. The blood normally contains substances called *opsonins* which, as it were, whet the appetite of the phagocytes, so that they can eat the bacteria in bunches instead of singly.

The aim of the chemist, and of the physician for that matter, is to destroy harmful bacteria. There are probably less bacteria suspended in the air than one would suppose, owing to the sterilising action of the ultra-violet rays from the sun. The ideal antiseptic for infected places in the body is one that will assist the serum to repair the tissues and at the same time kill invading pus bacteria and not the phagocytes. Pus bacteria cause abscesses, blood infection and blood-poisoning; they are the bacteria the surgeon dreaded before the days of antiseptic surgery. To combat them a selective chemical substance is required which will poison the protoplasm of the bacteria, but be perfectly innocuous to the body cells. Many of the older antiseptics, such as carbolic acid, mercuric chloride and iodine, are effective from the point of view of sterilisation, but they attack the surface cells of the body and delay healing. They are suitable for local infections, for washing out wounds or for the treatment of spreading infections, but they cannot be injected into the bloodstream to treat a generalised infection such as blood-poisoning. They would coagulate the body fluids. Even when applied locally they have little power of penetration and do not kill the bacteria that have invaded the tissues.

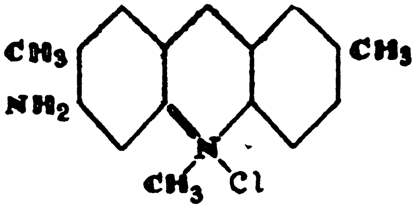
Clearly, a new range of antiseptics was required. Chemistry came to the aid of medicine. The antiseptic properties of chlorine have been known since Scheele discovered it in 1774, but it is too irritating in the free state to be of value in the healing art; on the other hand its irritating effects were utilised during the war, when it was employed as a poison gas. In the form of Dakin's solution (sodium hypochlorite) it was widely employed in the treatment of wounds. Dakin himself improved upon this by preparing organic antiseptics containing chlorine that were less irritating, and that slowly evolved chlorine in the tissues. These new chlorine compounds, the *chloramines*, were used for irrigating wounds so that they could be closed by suture instead of waiting for the wound to heal on its own account. *Chloramine-T*, a chemical definitely invented for the needs of medicine, is made from a by-product obtained in the manufacture of saccharin, a sugar substitute.

Paul Ehrlich, who died in 1915 while working on the synthesis of chemical specifics for the conquest of disease, compared the blood stream to a river containing a variety of fish, the problem of the chemist being to find a substance which when introduced into this stream will kill the obnoxious and unwanted inhabitants without affecting the normal ones. Ehrlich directed his attention towards the effect of dyes on living cells. He noted that they stained particular kinds of cells and left others untouched. Would they destroy the bacteria and parasites of disease and leave the ordinary cells of the body untouched? Gentian violet, brilliant green (related to malachite green, p. 276) and some of the triphenylmethane dyes were found to have decidedly antiseptic properties, acting selectively on bacteria and not appreciably on human cells. What is even more remarkable some dyes act selectively on different kinds of bacteria, slaying some and sparing others. Ehrlich's ideal antiseptic was one that was so potent against disease bacteria and so innocuous to man, that a single dose would kill the bacteria without harming the tissues. In practice even the most successful antiseptics fall short of this ideal.

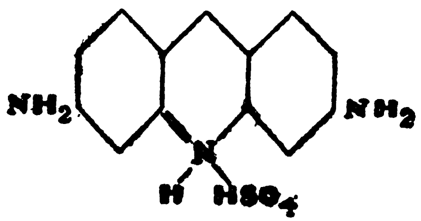
During the course of investigations on the therapeutic uses of dyestuffs Ehrlich found that *Acridine yellow,*



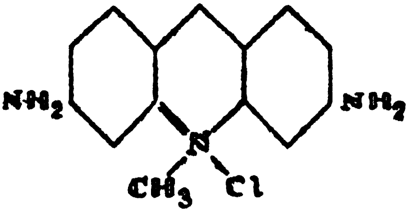
has a selective action on the deadly trypanosomes causing sleeping sickness. After many failures he found several dyes that produced a cure when injected into mice carrying the disease, but the results with human sleeping sickness were rather disappointing. Some of these dyes, such as *Trypan red* and *Trypan blue*, were found to be effective in the treatment of certain diseases of dogs and cattle (Texas fever). We have seen how the physiological action of certain molecules can be altered by chopping groups off, and by modifying existing groups and by introducing others. Now Ehrlich, in conjunction with the bacteriologist Bechold, discovered that whereas chlorine increases the antiseptic powers of some dyes, the methyl group decreases it. He therefore introduced a chlorine atom into Acridine Yellow, thereby obtaining *Acridinium yellow*,



a dye with increased bactericidal action, and then by a series of intricate chemical manœuvres cut out the methyl groups. The resulting dye was *Proflavine*—

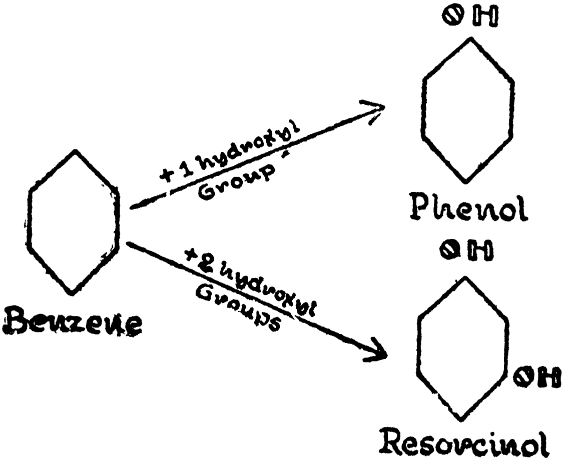


It was highly antiseptic, although in Ehrlich's opinion it fell short of the ideal. It contained no chlorine, and remembering the antiseptic action of this element when introduced into organic compounds, Ehrlich replaced the H and HSO_4 by a chlorine atom and a methyl group. He called the dye produced *Trypaflavine*—



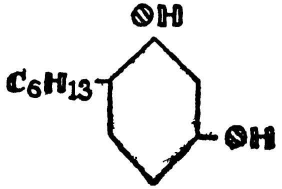
It was successfully employed as an antiseptic during the war and as a preventive of trypanosomal infections in animals. The dye is usually known in this country as *Acriflavine.* Gentian violet and acriflavine can be given internally or injected into the blood to prevent infection.

Remarkable results have been achieved by combining the penetrating power of aniline dyes with the antiseptic properties of such elements as mercury, which possess no power on their own of passing through the tissues. One of the most widely known and highly successful of these is *Mercurochrome,* a compound of mercury and the dye *Fluorescein.* Fluorescein has great penetrating power, but little or no antiseptic action; mercury is strongly antiseptic but has no penetrating power. The properties of both dye and mercury are combined in



mercurochrome. It destroys bacteria, or at any rate prevents them from multiplying, but does not injure the human host upon which the bacteria would live if they had the chance.

Fluorescein is derived from the coal-tar product, resorcinol, which has a mild antiseptic action. Resorcinol is obtained on a technical scale from both phenol (carbolic acid) and benzene; as shown on page 349 it is phenol with an extra hydroxyl group (OH). In 1921 Johnson and Hodge discovered that the antiseptic power of resorcinol could be increased by introducing methyl and ethyl groups, the products formed being at the same time relatively non-toxic towards the tissues. The effect of introducing other groups was observed and these investigators found that the maximum bactericidal power was reached in hexylresorcinol, that is resorcinol containing a hexyl group (C_6H_{13})—



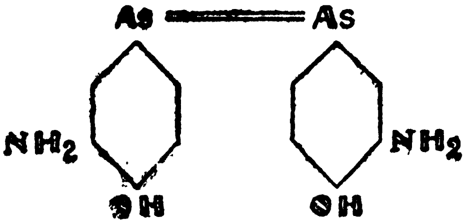
Hexylresorcinol is fifty times as powerful as carbolic acid, and at the same time it is non-toxic even in large doses. It forms an ideal internal antiseptic, that is, it can be administered by the mouth without its antiseptic qualities being destroyed by the body fluids, whilst at the same time it has no irritant or toxic action on the tissues. This synthetic antiseptic is another creation of the chemist, designed to destroy bacteria but not human cells. It renders the kidneys and urine free from infection, and is thus particularly useful in the treatment of kidney and urinary disorders. Hexylresorcinol has superseded the compounds of formaldehyde as an internal antiseptic. Previously formaldehyde, which is a powerful antiseptic, was administered either in combination with milk sugar (*formamint*) or with ammonia. The compound of formaldehyde and ammonia known as *hexamine*, or *urotropine*, was widely used as a urinary antiseptic.

During the present century attention has been focussed upon the preparation of specific drugs to cure specific diseases. Until comparatively recently very few specific remedies were known. It was recognised that cinchona owed its anti-malarial properties to quinine, which slays the malarial parasites but not the body cells, and that *ipecacuanha* is of value in the treatment of tropical dysentery by virtue of the drug *emetine* that it contains. Emetine is a specific against the organisms of this disease. Mercury preparations have also been used since the time of Paracelsus for the treatment of syphilis, the civilised man's greatest enemy. At the beginning of the present century the "chemotherapeutic" movement came into being. The term chemotherapy is rather difficult to define; it is that department of pharmacology dealing with the relation between the chemical structure of chemical remedies and their effect on living beings. Ehrlich, who initiated the study of chemotherapy by his researches on antitoxins, originally used the term in reference to infectious disease. For him the problem of chemotherapy was to prepare a substance capable of selective or specific action, that is, one that would destroy disease microbes without harming the cells of the body. Ehrlich showed that antitoxins constitute a defensive chemical mechanism against parasitic micro-organisms and their toxins, but are harmless to the body cells. He compared the antitoxins to magic bullets, charmed to fly at their objective, the invading micro-organisms and their toxins, and to do no damage elsewhere. Could not substances be prepared in the laboratory with a specific action against disease organisms?

We have seen how Ehrlich discovered that certain organic dyes had a special affinity for certain living cells and organisms, and that some of these dyes were specific for microbial parasites infecting rats, dogs and cattle. Now it has always been accepted that a given organic chemical has a certain definite physiological action. By introducing different groups into the substance and eliminating others, it is possible to make derivatives which are more potent in their physiological effects and yet less toxic to the body. The problem of chemotherapy as applied to microbial disease is to prepare a substance highly toxic to the parasite but with a minimum toxic effect upon the host.

Ehrlich's work on dyes laid the foundations for his work on the syphilitic specific, *salvarsan*. In 1863 Béchamp prepared a substance by the action of arsenic acid on aniline and experiments made with it at the beginning of the century showed that it was much less toxic than the ordinary inorganic forms of arsenic. For this reason it was called *atoxyl*. Lavaran, the discoverer of the malarial germ, showed that inorganic arsenic compounds check the infection of mice by trypanosomes, which are organisms related to those causing syphilis. In 1903 Thomas in England showed that atoxyl was even more effective, producing cures in infected mice. This discovery led to the organisation of an expedition under Koch—the discoverer of the tuberculosis bacillus—to Africa, where is was proposed to try atoxyl as a specific for sleeping sickness, a disease also caused by trypanosomes. The results obtained were very encouraging, although those treated suffered from objectionable after-effects, such as injury to the eyes.

In 1905 Fritz Schaudinn isolated the syphilis parasite, *Spirochaete pallida*, and showed that it is a trypanosome. This directed the attention of Ehrlich towards the treatment of syphilis by arsenic compounds. Assisted by the German dye works and by a group of collaborators, he prepared a large number of arsenic organic derivatives, and tested them on animals inoculated with the trypanosomes of human syphilis. Ehrlich looked for a *therapia sterilisans magna*, that is a substance, one dose of which would be effective. This has never been realised. In 1909, after he had tested six hundred and six organic arsenic derivatives Ehrlich introduced salvarsan as a specific against man's greatest scourge. It was put on the market in 1910 as "606". Not only did it effect a cure in many cases, but it prevented the spread of the disease from one person to another. Salvarsan is



Neo-salvarsan, a soluble form of salvarsan, was also produced in Ehrlich's laboratory and it has been found to be more satisfactory. Other similar organic arsenic compounds, such as *sulpharsphenamine* and *stovarsol,* have been used in the treatment of syphilis. Another valuable arsenic compound, *tryparsamide,* first prepared at the Rockefeller Institute for Medical Research, is used for treating syphilis of the central nervous system and for the treatment of the dreaded African sleeping sickness. Loevenhart and Lorenz, of the University of Wisconsin, discovered that tryparsamide is of value in curing general paralysis.

The dye and drug industries are closely connected, and in Germany the big dye firms have always been the first to appreciate the discovery of new synthetic drugs. Just before the war several German investigators had been working along the lines proposed by Ehrlich and the fruits of their research appeared in 1920 when the big German chemical firm, Bayer, placed 'Bayer 205' on the market. This substance, the exact composition of which has been kept a trade secret, is specific against African sleeping sickness. In 1926 another of the large German dye firms perfected a new synthetic organic chemical as a specific against malaria; it was called *plasmochin.* The discovery of these two new specifics marks another milestone in the development of chemotherapy.

For many years chaulmoogra oil has been used as a specific against leprosy, the dreaded disease of the East, which is caused by parasitic bacteria. Chaulmoogra oil is obtained from the seeds of certain tropical plants, but it cannot be administered in large doses because it is too irritant. Chemists have found that the oil owes its healing power to two acids which can be isolated from it. Much success has been achieved in the treatment of lepers by using a compound of these acids with alcohol. Mercurochrome has also been employed.

Attempts have been made to cure tuberculosis by chemotherapeutic means. The conquest of this disease must ultimately be achieved by hygienic measures—good and clean food, fresh air and tubercular-free milk—but in the meantime attempts have been made to prepare tuberculosis specifics. Koch found that certain gold compounds inhibit the growth of tubercle bacilli, and quite recently a gold compound called *sanocrysin* (gold sodium thiosulphate) has been introduced for the treatment of tuberculosis. It is a compound of gold and photographer's " hypo ". The search for a pneumonia specific has, so far, been rather disappointing. A German investigator, Morgenroth, found that the chemical *optochin*, a relation of quinine, improved the condition of tubercular mice. Unfortunately doses sufficient to kill off the bacilli in human beings had a strong toxic action on the optic nerve. Similar results were experienced with the dye, *proflavine*. More recently, however, experiments at Johns Hopkins University, U.S.A., show promising results with mercurochrome.

Bio-chemists and physiologists have devoted considerable attention to the study of glands, the organs of secretion. The glands of the body may be either provided with ducts, or they may be ductless or *endocrine* glands. The glands provided with ducts pour their secretions into some space outside the body tissues; they are glands of external secretion. Thus the digestive juices are poured into the stomach and intestines; the sweat glands pour a fluid on to the surface of the skin and the salivary glands supply saliva to the mouth. On the other hand the endocrine glands pour their secretions directly into the blood, and these are carried to all parts of the body. They are therefore known as the *internal secretions*. They contain specific compounds or *hormones* (chemical messengers) which circulate in the blood and produce remarkable changes in various parts of the body. They exert powerful actions on the processes of growth and activity in the tissues, and exert stimulating actions not only on particular organs but on the whole body. They are highly potent drugs and act in extremely minute amounts. Adrenalin, for example, the hormone of the suprarenal glands just above the kidneys, influences some tissues at a dilution of 1 in 300,000,000. This degree of dilution would be reached if one ounce of adrenalin were dissolved in the contents of forty miles of water carts, each holding 625 gallons, with 200 carts to the mile. Or take thyroxin, the hormone of the thyroid gland. Only three and a half grains ($\frac{1}{115}$ oz.) are needed in the human body in a year. It would appear from the small amounts of hormones needed by the body, that they act as catalysts, speeding up the metabolic processes.

The physiological study of the suprarenal glands dates from the middle of last century when Addison associated a form of general anæmia with a diseased state of the glands. Some forty years later Oliver and Schafer demonstrated that an extract of the suprarenals contains a substance that, even in minute doses, causes a rapid rise in blood pressure, an effect opposite to that produced by their removal. A search was made for a specific chemical responsible for these effects and in 1897 Abel and Crawford isolated a derivative of the suprarenal hormone. This hormone was prepared in the free condition by Takamine in 1901 and named *adrenalin*. It is now also known as *epinephrin*. The chemical constitution of adrenalin was worked out in 1904 by Jowett and shortly afterwards the compound was synthesised. Adrenalin, which is a drug of extraordinary potency, now occupies an important position in the medical armoury. Its physiological role in the body seems to be connected with the control of blood pressure and with the excitation of what is termed the sympathetic nervous system. The hormone is used in medicine for relieving spasms of acute bronchial asthma; for heart failure and circulatory weakness; for neutralising the effects of an overdose of insulin; and owing to its powerful action in constricting the capillaries, adrenalin is used in surgery to check bleeding. It permits of bloodless operations on the eye, and used in conjunction with the cocaine local anæsthetics prolongs and intensifies the anæsthesia. Many synthetic derivatives of adrenalin have been prepared and are now being used in place of adrenalin itself.

The drug *ephedrine*, which is chemically related to adrenalin, is sometimes used as a substitute for the latter, although it is not so potent. The clinical use of the plant from which ephedrine is extracted—a species of *Ephedra*—dates back to 3000 B.C. when, under the name of Ma Huang, it was employed by Chinese physicians. In 1887 two Japanese chemists, Nagai and Hori, isolated the drug in the pure form. It was not until 1917, when its chemical properties were examined more closely, that its clinical properties were re-investigated in the East. In 1923 synthetic ephedrine was introduced to the Western World. Unlike many drugs it can be administered orally.

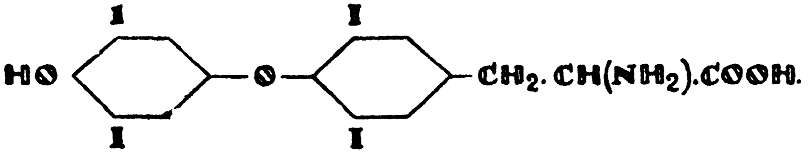
Recent work has shown that a close relationship exists between the outer or cortical cells of the suprarenal glands and sexual development. Some chemical substance or hormone from these cells controls normal sexual development, and if the cells are too active or develop tumours, remarkable sex changes occur. Mental and physical sexual precocity may result on the one hand, or a marked tendency towards masculinity on the other. Cases are not unknown of well-formed girls suddenly undergoing what almost amounts to a change in sex. They lose their feminine characteristics and assume those of the opposite sex. This change is due to the growth of a tumour on the cortical cells of the suprarenals, which throws the hormone balance out of gear, upsets the chemical secretions of the sex glands, and causes male characteristics to develop. Such individuals are the victims of a glandular mishap.

Adrenalin is responsible for the response of the body to violent emotions, such as courage, anger, cowardice and fear. When we get angry or aggressive, our blood pressure rises, we get hot, red in the face, and our heart beats faster. This results from the sudden liberation of adrenalin from the suprarenals. The fiery man has no control over his secretion of adrenalin; the even-tempered man has it well under control. We are only what our glands make us; we are but the products of our internal chemistry.

Another ductless gland that has been widely investigated is the thyroid, situated in the neck. The function of this gland in maintaining the health of the body has long been known. Its enlargement occurs in the disease known as goitre, which results from a lack of iodine in food and drinking water. The small quantities of iodine necessary to maintain the thyroid are derived from the soil on which we ultimately depend for our food. The thyroid has the power of concentrating the minute traces of iodine in the food and of using it for its own requirements. Iodine is present in the sea spray that is borne inland for considerable distances by the wind, and by this means the soil is being constantly replenished with small amounts of this necessary element. Consequently the soil of sheltered countries cut off from sea breezes is lacking in iodine, and it is in such countries that diseases associated with the thyroid are particularly prevalent. Goitre is very common in Switzerland and in the central states of U.S.A. After the introduction of antiseptic surgery in the last century, the thyroid was removed surgically and it was found that persons deprived of this gland become abnormally slow in movement and intellectual response. Their temperature is low, the pulse is slow, the muscles are torpid, and there is a general inability to perform the finer muscular movements. The skin thickens and swells and the individual becomes very dull mentally. When the thyroid of a child is removed, or when the gland is imperfectly developed, the child's growth is stunted, it remains childish in mind and body. These conditions were recognised as those accompanying the disease, common in Switzerland and other parts of Europe, known as *cretinism*. The unfortunate victims of this disease are known as *cretins*; they are stunted, sometimes goitrous, and almost imbecile.

When it was realised that the thyroid played such an important part in maintaining general health and development, attempts were made to see if the thyroids from slaughtered animals would cure or improve sufferers from goitre and cretinism. The results obtained were very satisfactory. The bio-chemist came to the assistance of medicine by preparing thyroid extract. Then in 1895 came Baumann's discovery that thyroid contains a relatively large amount of iodine, far greater than is contained in any other tissue in the body. This discovery was of fundamental importance in unravelling the physiology and pathology of the thyroid gland. Baumann showed that the iodine was firmly combined with one of the proteins of the thyroid to form a compound which he isolated under the name of *iodothyrin*. Attempts were made to isolate the iodine-containing substance responsible for the physiological activity of the thyroid, but they failed. It was not until 1915 that Kendall of America isolated the active principle of the gland and he named it *thyroxin*. It contains 65 per cent of iodine. Experiments show that without thyroxin, the hormone of the thyroid, the chemical processes of the body and even life itself are very sluggish. Thyroxin hastens the rate of chemical reaction on which muscular and mental activity, growth, glandular secretion and the heart beat depend. Those with not enough thyroxin are living too slowly; those with too much—and there are people with over-developed or hypertrophied thyroids—are living too quickly. The person with not enough thyroxin is usually slow, lethargic and fat. The fire of life burns slowly within him. On the other hand the person with too much will be restless, excitable, the heart beat will be rapid, and there will be a tendency towards thinness. Owing to the prevailing fashion of slimness among women, thyroid extract has been used for the slimming of the obese, and with disastrous results unless under expert medical guidance. Not only does it encourage the burning up of fatty tissue within the body, but it burns up the essential substances such as proteins and at the same time hastens all the metabolic processes. It acts like a pair of bellows on a fire. Too much thyroid or thyroxin increases the appetite and is responsible for the disease known as exophthalmic goitre, or " pop eyes " as the Americans call it.

Thyroxin has been studied in this country by Harington, and in 1926 he showed that it possesses the structure



In 1927 he synthesised it in the laboratory from coal tar products, and although the process is a long one synthetic thyroxin is cheaper than the natural product obtained from the thyroids of slaughtered animals.

In addition to the thyroid there are small glands embedded in it known as the parathyroids. Bio-chemists have shown that if they are removed tetany results. They appear to be intimately associated with the calcium balance in the body. The hormone secreted by these glands, which has not yet been obtained in a pure form, regulates the calcium content of the blood. Calcium is needed for the formation of bone and teeth.

Then we have the internal secretions from the pituitary gland, a small structure weighing about half a gram, situated in a groove at the base of the brain. Although no definite chemical compound has been isolated from the gland, an extract can be obtained from it with powerful physiological properties. It will cause contraction of the involuntary muscles of the body and for this reason pituitary extract (pituitrin) is injected in child-birth to stimulate the contractions of the womb. The secretions of the gland appear to accelerate growth processes. But what is the active substance present in the pituitary, and whether this gland secretes more than one active substance, cannot be answered at present.

In the normal process of digestion the sugar and carbohydrates of the food are mainly converted into glucose, which passes into the blood until its concentration in the latter reaches between 0·12 and 0·15 per cent. Any excess of glucose is stored in the liver in the form of a compound, something like starch, called *glycogen*. The glucose in the blood is gradually oxidised or burnt up, ultimately to carbon dioxide and water, and the heat resulting from this oxidation supplies the living body with energy. When the glucose in the blood falls below about 0·12 per cent, the glycogen in the liver is split up into glucose by an enzyme, and this fresh supply of glucose passes into the blood. There are some people who suffer from diabetes, that is they cannot use the sugar and carbohydrates present in the foods of a normal diet. These substances are not burnt up and circulate in the blood until the kidneys filter them off into the urine as waste products. But the combustion of sugar in the body is in some way related to the c[illegible]n of fats; both produce carbon dioxide and water. Bo[illegible]s of substances maintain the living fire within us. If [illegible]r is not being burnt properly as in the case of the diabetic, then the fats are also burnt imperfectly, and instead of being oxidised to carbon dioxide and water, the oxidation is only carried half way, with the result that poisonous acids are produced. These circulate in the blood and are a greater source of trouble to the diabetic than the mere loss of sugar. We might say that as long as the sugars burn brightly in the body the fats are consumed without trace. But if the sugar fire burns low the fats smoulder and produce a harmful smoke—the poisonous acids. These poisonous products accumulate and cause the auto-intoxication of the diabetic, so that unless the complaint be treated collapse and death finally occur. What is more, since the diabetic can get little or no energy from his sugars and fats, his body cells try to utilise the proteins of the food and of the tissues themselves. These proteins are partially resolved into sugar but it is of no use to the sufferer; it shares the fate of the food sugars that they cannot utilise. Now the normal function of the proteins is to build up and maintain the protoplasm—the " living stuff "—of the tissues. Consequently the diabetic in addition to being poisoned, gradually wastes away.

The first step towards an understanding of the cause of diabetes was taken as far back as 1683 when a physiologist named Brunner noted that the removal of the pancreas, or sweetbreads, of a dog was followed by symptoms now recognised as those accompanying diabetes. But Brunner failed to grasp the importance of his discovery. Little advance was made for two centuries until two German investigators, Minkowski and von Mering, discovered in 1889 that the removal of the pancreas is accompanied by the appearance of an abnormal amount of sugar in the urine. Like many other discoveries, this was a purely accidental one. The urine, which was not suspected to contain more than the normal amount of sugar, was allowed to dry up, and a mass of smal[illegible]emained. These attracted the attention of an inquisit[illegible]atory attendant who found that they had a sweet tast[illegible]is discovery, coupled with the observation by pathologists that patients who die of diabetes invariably possess a diseased or abnormal pancreas, caused diabetes to be associated with some deficiency of the pancreas.

Since the pancreas pl[illegible] an important part in digestion it appears at first sight [illegible] perhaps diabetes results from the failure of the pancrea[illegible] secrete digestive juices for the conversion of sugar into a form that the blood can oxidise. This view can be disproved by just tying the duct of the pancreas, so that while the gland remains intact and uninjured, its juice cannot flow into the intestine. Although such an operation causes a diminished power of digestion, the symptoms of diabetes do not appear. Similarly the pancreas can be removed and grafted to another part of the body without diabetes resulting, in spite of the fact that it cannot carry on its normal digestive functions. The evidence that the pancreas secretes something into the blood that promotes the burning up of sugar became so strong that in 1916 Sir Sharpey Schafer suggested a definite name for the substance. This he called *insulin*. Physiologists were thus convinced that insulin existed long before it was actually isolated. It was clearly another case of an internal secretion or hormone regulating one of the body functions. The evidence in favour of such a view was purely circumstantial, and the earlier attempts to obtain a pancreas extract containing this hormone were unsuccessful. Gradually it was realised that in extracting the pancreas, digestive ferments were extracted as well as the hormone and that they destroyed the latter.

Two Canadian physiologists, Banting and Best, overcame this difficulty by tying off the duct through which the pancreatic juice is poured into the intestine. This caused the cells producing the digestive juice to degenerate but did not interfere with the insulin-producing cells. In 1921 they prepared a potent extract from the pancreas of an animal treated in this way and found that injections of the extract relieved diabetic patients. In 1922 the same investigators, with the assistance of Collip, of McGill University, Montreal, were able to isolate a whitish powder from the extract. This was insulin. The original method of preparation was too complicated to make insulin on a manufacturing scale and so another method was devised. Ordinary slaughter house pancreas is extracted with dilute alcohol, which leaves the digestive ferments in the pancreas but extracts the insulin. Abel, of Johns Hopkins Medical School, has more recently prepared the hormone in the form of minute colourless crystals.

Insulin can never cure diabetes; it can only relieve it by replacing the insulin that the pancreas of the diabetic cannot manufacture. It has to be injected under the skin by means of a needle, because if administered by the mouth the digestive juices of the stomach destroy it before it reaches the blood stream. Insulin assists the tissues to burn sugar, but exactly how we do not know. It probably converts it into a form that is readily oxidised by the body cells. Great care must be taken in its administration. If too much is given it causes a rapid fall in the sugar content of the blood, with the result that eventually the nervous system ceases to function, convulsions occur and the patient collapses. Too much insulin is just as bad as too little. The dose of the hormone must therefore be carefully regulated; it depends upon the condition of the patient and the amount of sugar in the diet. If too much is given the harmful effects can always be counteracted by an injection of glucose. These harmful effects can be utilised in finding the strength of a particular insulin preparation since it cannot be weighed out or measured in a pure state. The strength of an insulin preparation is measured by observing the effect of a known amount on some suitable animal, such as a rabbit. An insulin unit is the amount that will reduce the glucose of an animal weighing 2 kilos (4·4 lbs.) to such an extent that convulsions occur in three hours.

Insulin has done much to relieve the suffering of diabetics, who, if left untreated would be condemned to a slow, lingering death. Even three injections of insulin a day are preferable to slow death. Many a sufferer on the threshold of death has been reclaimed, and in the case of children, in whom the diabetes runs an acute and fatal course, insulin has worked wonders.

As yet we do not know the chemical constitution of insulin, much less its synthesis. We are still dependent upon slaughtered animals for it. But synthetic substances having the properties of insulin, i.e. producing a lowering of the blood sugar have been prepared. They are derivatives of guanidine (amino-amyl-guanidine and amino-butyl guanidine), which is itself a derivative of urea. Small amounts are apparently efficacious, but the effects are produced very slowly. Although they may prove suitable in mild cases of diabetes, they are too slow for bad cases.

The reader should now possess some idea of the place of chemistry in the combating of disease; how the chemist isolates the naturally occurring drugs, works out their chemical constitution and synthesises them in the laboratory; how he can synthesise new products even better from the point of view of their physiological action than the naturally occurring ones; how specific chemicals can be produced to cure specific diseases; and how the bio-chemist has shown that we are what our glands make us. Even mentality can be improved by gland treatment. Will the day come when our personality will be controlled by a tablet out of a bottle? Will the bio-chemist change the nature of man—let us hope for the good—by the application of his potent synthetic drugs?

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